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Edible Oil Processing from a Patent Perspective

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Piæ memoriæ parentium[1]

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[1] In 1965, I dedicated my PhD thesis to my parents because genetically, educationally, and financially they had enabled me to attain this degree. Now, I dedicate this monograph to their memory because what they left me provided me with the necessary freedom to write it.

Preface

Patent literature has always been a mine of scientific and technological information. But as with minerals, some information lies near the surface and is easy to extract from opencast mines, whereas other information lies hidden deep under the ground and requires a lot of digging. Formerly, when I still lived in Belgium, it was deep mining. The only way to consult the patent literature was to take an early train to Brussels, walk to the Ministry of Economic Affairs, and go to the reading room. European patents and recent US patents were available on CD-ROM, most French patents on microfiche, and those I could consult myself after I had learned how to operate their reading equipment. Most other patents were only available in print, and getting hold of them meant writing a chit, handing it to the reading room supervisor, and waiting while somebody searched for the volume containing this patent in the catacombs under the ministry building. When he found it, he would put it into a small service elevator to the reading room, where I collected it, read the patent I was looking for, and made a photocopy. At the end of the afternoon, I would count the number of photocopies I had made that day, pay for them, and travel back home by train while studying the day's harvest.[1]

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[1] By now, the reader may have noticed that the above has been written in the first person rather than in the third person, which is more common in textbooks. I decided to use the first person for a number of reasons:

- Formerly, scientific articles were written in the first person. When I translated the first ever book on the chemistry of oils and fats that was published in 1823 (Chevreul 2009), I consulted books and articles written in the nineteenth century and noted all were written in the first person. I do not know when and why authors changed to the third person.
- Patents are still written in the first person, as illustrated by the quotation at the beginning of Chap. 5. Given the subject of this monograph, it is only logical to maintain that style.
- Apart from book chapters and articles, I write many letters and especially e-mail messages. The latter are in the first person and I prefer that style to referring to myself as "the author."
- Besides, this monograph has some autobiographical elements, which makes using the first person a natural choice.
- By writing in the first person, I can have freedom of speech and may express my opinion that what some author said is stupid. If I just wrote that what he said is stupid or that he was stupid, I could face a libel action.

At the end of the last century, this changed to opencast mining because websites such as http://be.espacenet.com, http://www.uspto.gov, and http://google.com/patents allow me to retrieve almost any patent from my desk, free of charge. Accordingly, patent literature is more easily accessible than most scientific journals. The Spanish oils and fats journal *Grasas y Aceitas* is now freely accessible through http://grasasyaceites.revistas.csic.es/index.php/grasasyaceites. Its French equivalent *Oléagineux, Corps Gras, Lipide—OCL*, which also carries many articles in English, can also be freely accessed at http://www.revue-ocl.fr, but the *Journal of the American Oil Chemists' Society* is only accessible to AOCS members who also subscribe to the journal. If not, you have to pay. I checked this out on an article I wrote myself (Dijkstra 1999). By searching for "stripping medium" and my surname, I retrieved the article through http://scholar.google.com and yes, it duly emerged. But: **Access to this resource is secured!** Adding the item to my shopping cart would have cost me $34.00.

Similarly, the *European Journal of Lipid Science and Technology* and its predecessor *Fett/Lipid* can be accessed through the web, but again, access is restricted. For people working at universities or large research institutes, access may be possible because their employer has bought some form of multi-user access, but for people working at home like myself, or people working in a refinery, a patent office, or a small company, purchasing articles can be too expensive. Accordingly, I now refer much more to patents in my articles and book chapters than before. I can easily get hold of them and so can my readers.

However, reading a patent and grasping its ins and outs requires somewhat different skills from what is needed to read an article in a journal (Dijkstra 2009). Accordingly, I will start this monograph by explaining what patents are all about. Not being a chartered patent agent myself, I will do this in layperson's terms and limit myself to what I think my readers need to know.

Things may have changed, but when I studied chemistry at university, nobody mentioned patents, and I am sure that the library of the chemical laboratory did not contain any patents either. To some extent, this is rather surprising since most of my professors had worked in industry before they were invited to become a university professor. I only came into contact with patents when I started to work for ICI.[2] I lunched with members of the patent department and I also made several inventions. For a few months I also shared digs with a patent trainee who later became a dear friend and who used me as sounding board when studying for his exams. But for me to be any use in this respect, he had to tell me a lot about patents first.

I found patents quite intriguing, and what I had learned came in extremely useful when I joined the Vandemoortele Group as R&D Director in 1978. This company was facing several infringement lawsuits, so the first thing I did was to consult this ICI friend, and together we designed a strategy. This involved opposing patents that had been granted to the company accusing us of infringement and taught me how to draft an opposition. Eventually, the strategy worked and the lawsuits were dropped,

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[2] ICI stands for Imperial Chemical Industries. When I joined ICI, it was the largest chemical company in the world, but now ICI no longer exists. What was left of it (the paints business) has been taken over by Akzo Nobel.

but the whole affair taught me that an elementary knowledge of patents and patent law is indispensable for R&D staff.

This indispensability was also highlighted when people in my department proudly reported that they made a breakthrough, which then turned out to have already been described in a patent. Instead of using this patent as a starting point and thinking of shortcomings and improvements, these people had wasted costly R&D time, and it was my responsibility to prevent this from happening again.

Since they had not learned anything about patents at university either, I started to provide them with some background information. As a result, they became much more patent-conscious. They started to consult patent literature and also recognized potential inventions in their own R&D work and organized this to substantiate these inventions. They were good pupils. When my department was disbanded, one of them pursued a career in intellectual property,[3] and another one introduced patent awareness in his new employment environment (Desmet-Ballestra) and introduced me as a consultant on intellectual property matters.

When introducing the world of patents, I will explain that individual patents may belong to a family of patents that started with a single application and developed into a number of subsequent applications in various countries and/or a number of granted national patents. As a rule, and provided it exists, I will refer to a publication in English and use the "(author, date)" system, where the "date" stands for the year of publication. This need not be the earliest publication since the application may have been published at an earlier date in another language.

If a patent document does not exist in English, its language will be clear from its title in the reference, with the exception of Japanese patent documents, where I will use the English title. Accordingly, I may refer to national publications in Swedish, Dutch, etc. and European applications that have been written in German or French. PCT[4] applications have a wider choice of languages (Arabic, Chinese, Japanese, Korean, Portuguese, Russian, or Spanish). If there is a US patent document in the patent family, I will in general opt for that one because US patents are so easily accessible through http://google.com/patents. If the PCT application does not have an English-language family member, it will have an English abstract that more or less explains what the invention is about. Japanese and other patent applications provided by Espacenet[5] also provide such abstracts, and those are the ones I use when discussing the documents concerned.

Subsequent chapters will deal with the various aspects of edible oil processing, such as production, refining, and modification processes. I will start most chapters

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[3] "Intellectual property" is a broader term than just patents. It also covers trademarks, copyright, and the like.

[4] PTC stands for Patent Cooperation Treaty, a union between countries that provides a unified procedure for filing patent applications. When these applications are published, their application number has the prefix WO.

[5] When accessed via http://be.espacenet.com, there is a choice of languages: Dutch, French, German, and English. When accessed via http://wordwide.espacenet.com, the choice of languages is even wider, but the site tends to switch to English when providing further information.

by summarizing the state of the art[6] around 1990. While doing so, I will not only refer to patents but also to handbooks and journal articles; with respect to the latter, I will limit myself to literature that is likely to be readily available within a company dealing with edible oils and fats.

After the summary of the state of the art, I will discuss individual granted patents and applications that have been published since 1990. However, I want to point out at this stage that I will only discuss a selection of these patents and applications. Consequently, this discussion should not be regarded as a full description of the prior art, and my not mentioning a patent does not mean there is no prior art. Readers can use my selection as a starting point, but if they want to make sure that an invention they made is novel or that there is prior art for a patent they wish to oppose, they should not rely on my selection: It is incomplete. Instead, they should carry out a novelty search themselves or ask a specialist to do so.

The object of this monograph is not to provide a complete overview of the patent literature but to describe and discuss recent developments in the field of edible oil processing from a patent perspective. In addition, I want to comment on whatever I read that strikes me as odd or that I consider to be a misunderstanding. When I consider literature to be biased, I will give another possible point of view. I want to identify contradictions and paradoxes and, if possible, suggest ways to resolve them. I want to highlight gaps in our understanding and hopefully suggest ways to fill them and thereby improve our understanding of edible oil processing.

Limiting myself to edible oil processing also implies that I had to be quite selective when working my way through the patent documents that emerged from a patent search. When gathering patent documents dealing with *Production of fats and oils from raw materials* (class C11B1 in the European classification system), I came across several documents that mentioned extraction only as a kind of afterthought. They dealt with plant breeding, genetic modification, how to grow algae in such a way that they accumulate a lot of DHA, and so forth. These are specialist subjects that are not of immediate interest to edible oil processors. Accordingly, I did not feed them into my literature database.

To summarize, I will discuss recent developments of edible oil processing by selecting certain patents that illustrate this development. I will discuss their content and occasionally also try to explain why I think that these patents and patent applications have been formulated the way they have and what prior art they had to take into account. European and US granted patents[7] list the documents that have been taken into account during the examination of the application on the front page. For applications, the European Patent Office publishes a Search Report with such a list.[8]

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[6] "State of the art" is typical patent jargon. The *Random House Unabridged Dictionary* describes this as "the latest and most sophisticated or advanced stage of a technology, art, or science."

[7] US Patent Application Publications with the year/number format do not list the literature search results.

[8] If the EP number is followed by A1, it means that a literature search report is attached to the application.

Selecting patents means going through a whole number of them and retaining those that hopefully serve the objects outlined above. Accordingly, I carried out a series of searches by consulting the Google patent website. This website has the advantage that it allows searches for patents issued during a specified timespan, such as 1990 to present; this is something you cannot do in Espacenet.[9] It also has the advantage that it provides patents as a pdf file, which makes printing this file faster than printing it page by page as required in Espacenet. A disadvantage of the Google website is that it is limited to US patents and patent applications. As mentioned before (Dijkstra 2009), this website is to be extended to non-US patents, but it is not clear when. Another disadvantage is that it does not recognize wildcards in classifications. So C11B1/* is not recognized, whereas in Espacenet, C11B1 is a valid search criterion that covers C11B1/00, C11B1/02, etc.

As I will explain in the next chapter, C11B/etc. stands for patent classes, and the tutorial mentioned in footnote 10 also explains the classification systems. I used them when collecting the patents referred to in this monograph. I had hardly used them before, and I must say I find them a bit cumbersome: There is no harmonization. Each national patent office decides itself how to classify an application it processes. Presumably, the patent office will look at the classes allocated by other patent offices, but it can only do so if these offices have already published their applications. So the allocations lack uniformity, and since the number of classes under which patents can be classified is not limited and can be very large, discrepancies result. In addition, any classification system is always out of date. Nobody can foresee what developments will require a class of their own.

Hence, in practice, I consulted both websites, selected those patents and patent applications I felt could be of interest, and printed the whole specification or just the front page and the conclusions. Then I assigned a file designation to them, introduced their particulars into my literature database, and filed the hard copies into my filing cabinets. Just compare this with having to travel to the Ministry of Economic Affairs in Brussels. Having moved to France, this would have been virtually impossible.

References

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[9] I recommend the tutorial in http://www.european-patent-office.org/wbt/espacenet/assistant; I found it quite useful.

Contents

Chapter 1
Introducing the World of Patents

1.1 General Background

When you go to university to study chemical engineering, you take several courses, take your exams, and when you finally graduate, you are a chemical engineer. You can work as a chemical engineer in your own country, and your degree is often recognized in other countries as well. With patents, that is quite different. Universities do not offer degree courses that allow you to become a patent agent. To reach that status, you will have to work your way through a kind of guild system. You will only be admitted into this system if you already hold a university degree in engineering or science, and in some countries you should also have some industrial experience. Then you have to find a tutor willing to accept you as his apprentice, familiarize yourself with the subject, become a mate to an associate, and finally, after having passed two or more examinations, become a master; only then may you put "CPA" (Chartered Patent Agent) after your name. Medical specialists and attorneys undergo a similar training by their peers.

Qualifying as a patent agent[1] allows you to represent inventors and practice before the patent office but only in the country where you signed the charter. That is because patents are national affairs and different countries deal with them in different ways. It is a bit like alcoholic beverage control in the United States: Each state has its own laws, and although they deal with the same subject, there are wide differences among individual states. I grew up in the Netherlands. At that time, the Dutch Patent Office was regarded as very strict.[2] Applications were published as submitted and then examined by the patent office; this might have led to a rejection of the application, its acceptance, or an amendment. The resulting text was again

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[1] In the United States, there are also patent attorneys. Patent agents have a scientific or technical background and attorneys have a legal background. The distinction is similar to that between a solicitor and a barrister.

[2] This may well be one of the reasons why the European Patent Office has a branch in Rijswijk near The Hague, which focuses on literature searches.

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published to give the general public an opportunity to comment, that is, to oppose the granting of a patent. Only if nobody opposed it or the patent office decided that the opposition lacked conclusive arguments would a patent be granted, published, and allocated a new number.

Compare this with the situation I encountered when I moved to Belgium, a country that had been part of the Netherlands in the early nineteenth century. In Belgium, the Ministry of Economic Affairs granted a patent after ascertaining that the application met the mandatory typographical requirements and the appropriate fees had been paid. There was no examination, no possibility to oppose, and the only way to find out if you should let the existence of this granted patent influence your actions was to ask a judge to agree with you that the patent should not have been granted. Two neighboring countries can be vastly different in their approach to patents.

Not surprisingly, these differences were also reflected in the way industry regarded patents. In the Netherlands, companies such as Philips, Shell, AKZO, DSM, and Unilever had their own patent departments, where they also trained their future agents, and there was a general awareness of patents and what they can do for you. In Belgium, the first thing you did when accused of infringement was to dispute the validity of the patent. This often worked, and so patents were regarded as more of a nuisance than an asset.

The word “patent” is an abbreviation of “letters patent.” It is derived from the Latin verb *pateo*, to open, to disclose, and this is exactly what a patent does. It discloses something an inventor or company would prefer to keep secret if it were not for the fact that the government has granted him the right to restrain his competitors from making use of what he has disclosed. So when granting a patent, a government in fact restricts competition but considers this to be justified because:

1. A patent is valid for a limited period only.
2. The disclosure of the technology will promote the development of science and technology.
3. It made money by charging a fee or even annuities.

I will come back to these aspects in due course.

So a patent discloses something, and that something is an invention. The word “invention” also stems from a Latin verb *invenio*, meaning to encounter, to come across. However, these meanings are most misleading indeed because they do not distinguish between a discovery and an invention, and that distinction is essential. A discovery refers to something that was already there but you did not know about.[3] Columbus discovered America; he did not invent it. A petrol company hopes to discover oilfields, but when it starts inventing them, it is time to sell any of its shares you might hold.

An invention, on the other hand, refers to something that did not exist already, something that is novel. An invention can refer to something tangible like a machine

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[3] That is why I find it difficult to accept that certain biotechnological findings qualify for patent protection.

(often referred to as an "apparatus" in patent jargon), but it can also refer to a process to make something or the use of an existing material or compound. However, novelty is not the only characteristic of an invention (Bloomer 2004a). If you build a new house that is somewhat different from existing houses, it is novel, but is there something surprising about that house? Probably not, so it is not really an invention. Accordingly, patent law prescribes that for a machine or process to be patentable, it should not only be novel, but there should also be some element of surprise and unpredictability in it, which element patent jargon describes as being "non-obvious for those of ordinary skill in the art." Accordingly, patent specifications often start the summary of the invention by saying, "Surprisingly, we[4] found …." In addition, patent law prescribes that to merit a patent, an invention should also be useful.

By granting patents for inventions, governments hope to encourage innovation and thereby promote economic activity and growth. They can pursue the same goal by granting patents for importing things a country needs but does not produce itself. Then these things are not novel in an absolute sense but novel for the country concerned. Nowadays, there are not many countries left that will grant patents of importation.

The Dutch word for "patent" is *octrooi*. The word stems from a French word (*octroi*), but to confuse matters, the current French word for patent is *brevet.* In the middle of the eighteenth century, one of my forebears, Abraham Ferwerda, bought an "octrooi" from the authorities that gave him sole right to publish a newspaper[5] in the province of Friesland. He obtained this right on the grounds that there was a need for a newspaper, but the province was too small to support two newspapers. So again, the novelty of that newspaper was not absolute, but it was novel to Friesland.

As mentioned above, a granted patent gives its owner the right to restrain others from making use of the invention. This has a fairly obvious implication: There cannot be two patents granted to two different inventors for the same invention. This raises the question of how to define an invention and which inventor should get the patent. How to define an invention is not only essential for the patent office examining the patent, but it is also of vital importance for people working in industry. They have to know what they are free to do and what action might lead to their being accused of infringement. Accordingly, I will discuss how to read and interpret a patent in quite some detail.

Earlier I mentioned "making use of the invention." What exactly does this mean? Does it prevent me from repeating an experiment (an example) in a country where the patent has been granted? Should I therefore go to another country where the patent is not in force to carry out my experiments? That would be against the spirit of national patent law, which, after all, aims at encouraging innovation in the country itself. "Making use of the invention" therefore assumes that this is for direct financial gain, that is, by selling the apparatus that is claimed in the patent or by selling the

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[4] This is an illustration of the use of the first person in patents.

[5] This newspaper is the *Leeuwarder Courant*, founded in 1752 and still published today.

reaction products that are made by the process according to the invention. Copying an example to see if it works or to produce a material for further testing is not for direct financial gain and therefore does not infringe the patent.[6]

Which inventor should get the patent is an aspect of patent law. As patents are a national affair, patent laws can differ between countries and they can also be changed. US patent law prescribes that the patent be given to the first person who thought of the idea underlying the invention ("First to find"). This obliges potential inventors to make sure that they can demonstrate when they made their invention; consequently, it involves notebooks with numbered pages and a stupendous amount of red tape.[7] As far as I am aware, US patent law is unique in this respect and all other countries determine which inventor gets the patent by looking at the filing date ("First to file"). An example of a fairly recent change in US patent law is the fact that the United States (referred to as "US" for short hereafter) now also publishes applications, whereas formerly the first (and only) document published was the granted patent. On the other hand, the US still does not allow the public to oppose granted patents as in Europe.

1.2 Reading a Patent

There are some similarities between reading a Latin or Greek text and reading a patent, especially its claims Bloomer (2004h). In both instances, sentences can be quite long, and finding your way in them requires some training. After having learned some grammar and vocabulary, I was instructed to tackle a Latin sentence by first looking for the verb. Its inflectional form would then give a clue as to the subject of the sentence and so on. Similarly, patents are full of jargon a reader must recognize as such, and claims always consist of a single sentence that can be quite long.[8] You do not tackle them by looking for the verb, since it is often lacking, but by analyzing their structure and searching for words like *characterized in that* or *in which* or *wherein* or *the improvement being.* And as with Latin, after having attempted a first translation, it is a good idea to go back and make sure you did not miss out on anything.

Published patent documents also have a structure. The title or front page provides administrative background information and an abstract. Granted US and European patents also list a bibliography on the front page. This bibliography contains the documents that have been taken into account when the application was

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[6] At this point, Dr. Scott Bloomer, a US patent agent who kindly reviewed my draft text, remarked that this may not generally be true in each country and may also change. He also advised me to add a sentence stating that nothing in this chapter should be construed as legal advice. Please note that.

[7] When I worked for Imperial Chemical Industries (ICI) in the 1960s in a research laboratory, I also had to use these notebooks just in case ICI wanted to apply for a patent in the US

[8] As pointed out when discussing a Spanish patent in the next chapter, Spanish claims do not necessarily consist of a single sentence.

examined; its entries can originate from the applicant as well as from the patent office that carried out the literature search. The next pages (the specification) describe the invention under more or less set headings in a certain order.

Like other legal documents, patents need their own jargon to ensure a lack of ambiguity. Accordingly, they contain words and expressions that are rarely encountered outside the world of patents. I have already mentioned the expression "a person skilled in the art," meaning a person who specializes in the field of the invention. I could refer to myself as "a person skilled in the art of processing edible oils and fats."[9] Another example of typical patent jargon is the expression "composition of matter," which refers to a type of invention claiming a certain compound or mixture of compounds.[10] A confectionery fat meeting certain requirements could be described as a composition of matter. And then there is, of course, the "prior art" or "state of the art," meaning all factual information that is relevant to an invention that has been published before a certain date. The term "prior art" itself can also be used in a stricter sense, and then it means a document that destroys novelty by describing the invention before it was applied for.

There are also words that in the world of patents have a far more precisely defined meaning than outside this world. Take the verb "to comprise," for example. According to the *Oxford English Dictionary*, this means "to consist of, be made up of" and the example given is "The country comprises 20 states." *Random House Unabridged Dictionary* lists "to include or contain; to consist or be composed of; to form or constitute."

In patent jargon, the verb "to comprise" has a different and highly specific meaning that can be defined as "consisting at least of." So in patent jargon, saying that the country comprises 20 states means that it can also contain autonomous republics, districts, you name them. They need not be there, but they may be. So an apparatus comprising parts A, B, and C can also contain parts D and/or E, whereas an apparatus consisting of parts A, B, and C only contains said parts and cannot contain other parts as well. This explains why the word "comprise" is often used in claims.[11] It permits a distinction between an open-ended description and an exclusionary one. Its use can be alternated with that of the verb "to include," as illustrated by the first step of a biodiesel process: "transesterifying a mixture of fatty acid esters of glycerol with a lower alkyl alcohol while using an alkaline catalyst to form a reaction mixture *comprising* glycerol, fatty acid lower alkyl esters, and undesirable amounts of haze forming particle contaminants *including* sterol glucosides."

In the previous section, I referred to "said parts." This use of the word "said" is also typical patent jargon, as confirmed by the *Oxford English Dictionary*: "used in legal language or humorously to refer to someone or something already mentioned or named." It is a synonym of "aforementioned." It is used to avoid ambiguity, but,

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[9] In US prosecution, a less specialized person can be referred to as "one of ordinary skill in the art."

[10] A Google Advanced Patent Search specifying "composition of matter" in the title led to close to 6,000 hits.

[11] It is also used in titles but causes difficulties as exemplified by Jakel et al. (2003), which includes products *compressing* corn oil.

actually, the meaning hardly ever changes when “said” is replaced by “the,” “this,” or “that.”And what about “same”? A patent title can read, “Sesame oil and process for producing same” (Miyake et al. 2007). I would prefer, “Sesame oil and process for its production,” and I see no reason not to follow this preference.

Another way to avoid ambiguity is by numbering items. So a chemical process can be carried out in a first reaction vessel, from which the reaction product is pumped via a heat exchanger to a second reaction vessel. If you then want to add an excess of caustic soda, you could continue the sentence – remember that claims always consist of a single sentence – with, “and an excess of caustic soda is added.” More precise is, “whereupon an excess of caustic soda is added to said second reaction vessel.” Items in a drawing can also be given numbers and then the text can refer to these numbers. Accordingly, the process is carried out in reaction vessel (1), from which the reaction product is transferred by pump (2) through heat exchanger (3) to reaction vessel (4), and an excess of caustic soda is added to reaction vessel (4). And so a concise and easily readable text becomes verbose and more and more cumbersome to read.

1.2.1 Front Page

The title page of all patents contains some factual background information such as, but not limited to (another patent jargon phrase), the patent number, the title of the patent, the country that granted the patent, when the application was filed, who made the invention, and so on. These categories have numbers in front of them. For example, a US patent may say:

(73) Assignee: **Council of Scientific and Industrial Research**, New Delhi (India)

The (73) is a number that has been agreed upon. The World Intellectual Property Organization (WIPO), a part of the United Nations, has issued standards on how to number the background information categories on the title page, how to abbreviate countries, and so forth (www.wipo.int/standards/en). These standards have been in operation since the 1970s, which means that older patents may list the same categories but without the number in front. I will now discuss several of these categories and compare how various patent offices interpret the WIPO guidelines. Above all, I will use this discussion to provide some background information on patent procedures.

[10] **Document identification**. This number can be used to identify published applications (in German, *Offenlegungsschrift*[12]). Since 2001, US patents have also

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[12] The German patent system has always published applications as filed, and they were called *Offenlegungsschrift* (In Dutch *Terinzagelegging*). The English language had no word for this and so described this publication as “German Laid-Open Publication,” which is a rather literal translation from the German. Similar Japanese applications have also been referred to as “Unexamined Patent Applications.” Now that the US and the UK publish applications and call them “(12) Patent Application Publication” (US) or “(12) UK Patent Application,” the German *Offenlegungsschrifte* can also be referred to as “Patent Applications” in English.

had the number [10] in front of the patent number, whereas in 2000, they still had the number [11].

Patent numbers can also have suffixes. European patent application numbers are always followed by a capital A and a number. In this context:

- A1 means that the published application includes a literature Search Report.
- A2 means that the published application still lacks a Search Report.
- A3 refers to the belated Search Report.
- B1 refers to a granted patent.
- B2 refers to a patent that had to be amended as the result of an opposition to the original B1 patent.

Since the US started publishing applications, a similar suffix system has been in force.

[11] **Patent document number.** As shown above, this number could refer to a US patent that was granted before 2001. The European Patent Office (EPO) uses this category for both published applications and granted patents. In fact, the whole numbering system strikes me as rather confusing. Patent offices give a number to applications reaching the office. US patent 7,226,771 (Gramatikova et al. 2007), for instance, received application number 10/796,907 when it was filed in 2004. When the application was published in 2005, it got another number: US 2005/0108789 A1, and the patent granted in 2007 got yet another number again. The EPO, on the other hand, uses the same number for the application publication and the granted patent, but the internal application number is different and reflects the year in which the application was filed with the EPO.

To get some understanding of the numbering systems, we should look at how patents are conceived and born. When an inventor decides he would like to have his invention patented, he files an application with a national patent office, usually but not necessarily in the country where he lives. This office then registers the date of filing as the priority date and gives the application an internal number. This number is called the “application number.” According to the Paris Convention, the inventor need not decide immediately in which other countries he would like to obtain patent protection; he has a year’s grace to decide. If he then decides within this year to file applications in other countries, the countries having signed the Paris Convention respect the priority date registered by the patent office where the inventor filed the first application. Accordingly, when examining the application, they will not take prior art into account that was published after this priority date but before the patent was filed in their office. This means that the other countries must be informed. So when applying in other countries, the inventor, or rather his agent, will claim priority by informing the patent offices concerned of the application number and filing date of the original application, also referred to as the “priority application.” If then, at a later stage, these countries publish the application and/or a granted patent, they will refer on these publications to this first filing date as the priority date and to the original application number as the priority number (International Identification [INID] number 30).

An example may help to clarify the above. Krupp Maschinentechnik GmbH collaborated with staff in the oil mill in Martfü, Hungary, to develop an acid refining process. On 23 August 1990, they filed a patent application in Hungary that was given number HU 529290. Within the priority year, on 14 August 1991, they filed a European application that was given application number 91113617.4 and published on 11 March 1992, that is, just 18 months after the priority date under number 0473985 A2 (Rohdenburg et al. 1992). The EPO published a search report (0473985 A3), and finally, a patent was granted (0473985 B1) on 7 December 1994. These European documents mention as priority (30) 23.08.90 HU 529290. In the US, Krupp filed a patent application on 22 August 1991, that is, just before the priority year lapsed, and a patent (US 5,239,096) was granted on 24 August 1993, which happens to be well before the EPO decided that the application was worth a granted patent. This US patent mentions its own internal application number 748,660 and also [30] Foreign Application Priority Data: Aug. 23.1990 [HU] Hungary 529290. The same data are also printed on the Hungarian patent (HU 208 037 B), which was granted on 28.07.93.

I do not speak Hungarian, so how do I know that this Hungarian patent was granted on 23 July 1993? That is where the categories come in very handy. Category [45] shows the "date of publication by printing or similar process of an examined document on which grant has taken place on or before the set date." On the printed Hungarian patent, I saw the date 23 July 1993 after category [45], so there we are. Similarly, the Hungarian patent (Rohdenburg et al. 1990) uses category "[21] A bejelenté száma: 5292/90" to indicate the number assigned to the application and "[22] A bejelenté napja 1990.08.23" to indicate the date this application was filed.

The above application was not filed with the World Intellectual Property Organization (WIPO) under the Patent Cooperation Treaty (PCT),[13] but Krupp could have decided to do so. This treaty allows applicants to file an application within the priority year and this application is then published 18 months after its priority date. The WIPO arranges a literature Search Report to be made by an International Searching Authority and also provides an International Preliminary Report on Patentability (IPRP). The applicant can then decide on the basis of this IPRP whether or not to enter national and regional phases; if this entry is within 30 months of the priority date, this priority is maintained. Consequently, the applicant can save money by not having to translate an application into several languages and pay several fees to national patent offices for applications that he would not have made if he had known sufficiently early that they were unlikely to lead to a patent. So the WIPO does not grant patents like the national offices and the European Patent Office (EPO), but facilitates the granting by providing an early evaluation (the IPRP).

In the PCT application, there is a category [81] listing the designated states. This list can include the EPO and the countries that can be designated in the European application. If the EPO finally grants a patent, it will notify the designated states, but

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[13] See also http://en.wikipedia.org/wiki/Patent_Cooperation_Treaty.

then it is up to the applicant to get the European patent validated in the various designated countries. This usually entails having the patent translated into the language spoken in those countries, and paying fees to the national patent offices, and can therefore be quite expensive. In this respect, Europe is at a clear disadvantage compared with the US.

Accordingly, there have been movements to arrive at a single European patent that would be valid across Europe without having to be translated into various languages. These movements have been going on for quite some time, but at the time of this writing, Italy and Spain are the main objectors. Some kind of compromise will no doubt be reached eventually, and then, at long last, a court in Latvia may have to discuss the validity of a patent written in French.

[12] **Type of document.** Under this category, US patents mention today that the document concerns a United States Patent; until 2001, they did not. European documents mention that it concerns a European Patent Application or a granted patent, and the language in which this is done is the same as the language used in the document concerned. So if [12] says, "*Europäische Patentschrift*" ("European patent"), the text will be in German, but the claims are also published in English and French.

[25] **Language of original document**. This sounds like a useful category, but while referring to the example given above, neither the US patent nor the European patent documents indicate that the original document was in Hungarian. At least, I assumed it was because it was filed in Hungary and most countries insist that any documents filed use the language (or one of the official languages) spoken in the country.[14]

[30], [31], and [32] **Priority data**. The European Krupp patent discussed above mentioned as priority (30) 23.08.90 HU 529290. Category [30] is defined as "priority data," category [31] as "Number given to priority application," and category [32] as "Filing date of priority document." Since most, if not all, counties now use the "first to file" system, the vital importance of these priority data is clear. Some countries also determine the life span of a patent by starting from its priority date; in the US, this is 20 years from the earliest filing date, but as patents are national affairs, the life span varies from country to country.

US patents are also subject to Patent Term Adjustment (PTA), by which the lifetime of a patent can be extended by as many days as the US Patent Office failed to take action within its own stated deadlines. The PTA can also be reduced by failure of the applicant to reply within certain deadlines, notably the 3-month "Shortened Statuary Period of Reply."

[43] **Date of publication**. The date of publication determines whether or not a patent document can be regarded as prior art for a later application by somebody else.

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[14] In Belgium, companies that are located in an area where the official language is French can only file applications that have been written in French; in Flanders, applications have to be written in Dutch.

It refers to the first time the public could read what the invention was all about. If the later application was filed before the date of publication of this patent document, the said document cannot be regarded as prior art.

[45] **Date of grant**. On the title page of US patents, the “Date of patent,” which means the date the patent was granted (issued), is printed just under the patent number in the top right corner. For some reason or other, that date is always a Tuesday (Bloomer 2004f).

[51] **International classification**. As mentioned in the Preface, all topics that may be the subject of a patent have been classified in the International Patent Classification (IPC), a system comprising sections (A, B, C etc.), a class (two-digit number), a subclass (letter), and a main group (one- to three-digit number) that is followed by a backslash and a subgroup. Accordingly, C11B7/00 stands for

C	CHEMISTRY; METALLURGY
11	ANIMAL AND VEGETABLE OILS, FATS, FATTY SUBSTANCES AND WAXES; FATTY ACIDS THERE FROM; DETERGENTS; CANDLES
B	PRODUCING (pressing, extraction) REFINING AND PRESERVING FATS, FATTY SUBSTANCES (e.g., lanolin), FATTY OILS AND WAXES, INCLUDING EXTRACTION FROM WASTE MATERIALS; ESSENTIAL OILS; PERFUMES
7	Separation of mixtures of fats or fatty oils into their constituents, e.g., saturated oils from unsaturated oils
00	This stands for a series of different separation processes listed as 00B, 00B2, … 00C, etc.

The IPC is used extensively when searching the patent literature. It also serves as the basis for the more detailed European classification system (ECLA). How to use them when searching the patent literature and searching in general is explained in detail at http://wordlwide.espacenet.com/help?locale=en_EP&method=handleHelpTopic&topic = index.

US patents also list IPC classes, but since these one or more classes have been assigned by the USPTO, they may differ from the classes assigned by other patent offices where an application has been filed such as the EPO. So what searching by classification yields may depend on the database. Espacenet may not list patents that are listed for the same search criterion by the Google US patents’ site.

[52] **Domestic classification**. This is used on US patents since the US operates its own classification system.

[54] **Title of the invention**. I consider this heading to be self-evident.

[56] **Prior art documents**. This list is the outcome of the literature search carried out by the appropriate patent office, the USPTO for US patents, the EPO for European patents. It is only printed on the title page of granted patents.

[57] **Abstract**. The abstract is submitted by the applicant. It may quote the main claim but usually describes the invention less formally than a claim, using more everyday words and less jargon.

[58] **Field of search**. US-granted patents list what classes have been searched to arrive at the references cited in [56].

[60]–[66] **References to patent history**. US patent 6,844,458 B2 (Copeland and Belcher 2005) has a rather checkered history as illustrated by the quotation of what its title page says under [60]: "Continuation-in-part of Application No. 09/776,477, filed on Feb. 2, 2001, now Pat. No. 6,441,209, which is a continuation-in-part of application No 09/550,375 filed on Apr. 14, 2000, now abandoned, which is a division of application No. 09/197,953, filed on Nov. 20, 1998, now Pat. No. 6,172,248."

[71] **Name of applicant of applicants**. In the US, the inventor or inventors apply for a patent and if they work for a company that pays for the application, they "assign, transfer, and sell"[15] their right to this company at the same time. In Europe, the company itself applies and is therefore mentioned as the applicant. If two or more companies apply jointly for a patent, all of them are listed. Self-employed inventors apply in their own name.

[72] **Names of inventors**. In the US, because the inventors are the applicants, they are most certainly listed. US patents are often referred to by the surname of the first inventor. However, how these inventors are listed has not been harmonized, not even within a patent office. In the US, they can be listed as *First Middle Last*,[16] *First M. Last,* or even *First Last*, omitting the middle name or initial. Whatever the choice, they also list *City, State* for inventors living in the US, or C*ity, Country* for those who do not. German patent documents also mention the inventor(s) since German law prescribes that inventors working for a company share in the proceeds. There the format is *Last, First, Title or Titles, ZIP code city.*

PCT application publications also list inventors and use the format *LAST*,[17] *First Middle, Street, ZIPcode City.* European patent documents also name inventors and do so according to the format *Last, First, ZIPcode City,* but they may also include titles and/or street names.

The above examples illustrate the lack of harmonization. The lack of verification can also lead to patents being assigned to non-existent persons. I noted on a previous occasion (footnote on page 296 of Dijkstra 2007) that the family members of

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[15] Because selling involves handing over money, ICI, my first industrial employer, gave inventors a silver dollar when they applied for a US patent. I liked this custom and tried to introduce the same tradition within the Vandemoortele Group. It was tolerated for the first two or three patents but then frowned upon as a waste of good money and discontinued.

[16] This is the way that ReferenceManager® (a software program I use as literature database and to generate the bibliographies at the end of each chapter in this monograph) describes the choice I have to make when formatting the bibliography settings. For this monograph, I chose for name order: *Last First Middle* and for initials *FM* to be in accordance with the guidelines of the publisher. Formatting the settings is a bit of work, but subsequently, generating the bibliography without typing errors is only a single mouse click.

[17] By using capitals for LAST, I indicate that PCT applications also use capitals when printing them.

EP 1 159 877 (Sahasranamam 2001) suffer from this problem. Its inventor is U.R. Sahasranamam, whose first given name is Ullanoormadam and his second is Ramasubramaniam. Most patents belonging to this family correctly list Sahasranamam, U.R., but the German patent (DE 601 12 179 T2) lists Sahasranamam Ullanoor Madam Ramasubramaniam, whereas US Application Publication 2005/0069620 only prints Ullanoormadam in the top left corner of the title page. This is also the inventor's name in US Patent 6,808,737, of which the said application is a division. The fact that the European Patent Office database gives Vasahalanaman as the inventor in the Chinese equivalent is caused by the fact that his name was first transcribed into Chinese and then back from Chinese to Latin characters.[18] In US patent 6,706,299 (Kaimal et al. 2004), the first inventor is T.N.B. Kaimal. Even so, the top left corner reads Thengumpillil et al., which is the given name corresponding to his first initial.

Accents also get a hard time from foreign patent offices and searches are complicated by their being treated in different ways. An inventor called Müller may retain his umlaut or lose it and become Muller, but if he feared it might get lost, he may have given his name as Mueller. This means that the search should specify: Müller OR Muller OR Mueller.[19] According to the European equivalent, the inventors of the Krupp patent discussed above in the section dealing with [11] *Patent document number* are Rohdenburg, Herbert; Csernitzky, Károly; Chikány, Béla; Perédi, József[20]; Boródi, Attila; Fábicsné Ruzics, Anna. In the US equivalent, all eight accents have been omitted and poor Anna is mentioned as Anna F. Ruzics, so do not expect to find her when searching for Fábicsné.

[73] **Names of assignees**. If you want to know what your competitor is up to, it is very convenient that patents nearly always provide the name of the company or body to which the inventors have assigned their patent rights (US) or that applied for the patent (Europe, for instance).

[74] **Names of patent agents**. There may be occasions when it is useful to know which patent office dealt with a certain patent. If you would like to obtain a license, a good person to approach is the patent agent.

Drawing. If a patent contains one or more drawings, the USPTO puts the most representative of these drawings on the title page. This often tends to be the first drawing. This category has no number.

The above list has been limited to those categories that occur most frequently on title pages, those that gave me an opportunity to provide some background

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[18] Transcribing into Japanese and back also leads to names that may be difficult to recognize. The bibliographic data provided by Espacenet for Japanese Published Patent Application JP5117685 mention a certain Aruberuto Yan Deikusutora as one of the inventors. That is me.

[19] Since Müller is quite a common surname, further search criteria are useful to reduce the number of hits.

[20] The European patent title page also has some typing errors: *J zsef* instead of *József* and *Bor di* instead of *Boródi.*

information, or those that can be used in patent searches. For a full list, the reader is referred to the WIPO website (www.wipo.int).

1.2.2 Field of the Invention

Except in US patents with one or more drawings, turning the front page brings you to the start of the body of the text that makes up the specification. Although there are no set and agreed rules that prescribe which headings to use in what order, there is a kind of silent convention or gentlemen's agreement about what kind of things to say where and when. Furthermore, within the various countries, there are customs of a typographical nature. US patents use two columns per page, whereas in Europe, a single column is common; even Great Britain, which formerly used two columns, has now changed to a single column. US patents print the patent number as header and the patent title above the first column, whereas in Europe, only the patent number is printed.

Another typographical aspect is numbering for ease of reference. Search reports may quote a passage by referring to column or page number so-and-so, and then line number such-and-such. Examiners do the same in their Office Actions[21] and patent agents in their replies. Today US Application Publications number paragraphs: "**[0001]**The present invention relates to a method …" (for instance, Dawson 2005a). In this system, the numbering of paragraphs stops at the claims since the latter have numbers themselves, whereas the numbering of columns and lines also applied to the claims. On the other hand, US-granted patents still number lines (Dawson 2005b). Personally, I prefer line numbering since it is more precise in pinpointing attention to a certain word or phrase.

So it is not uncommon to start a patent with outlining which areas of industrial activity the invention is concerned. The standard phrase to do so is, "This invention relates to …" and then the apparatus or process is described in very elementary terms. This can be under a separate heading such as *Field of the invention* or *Technical field,* or it can be incorporated as the introduction to the next heading, "Background of the Invention."

1.2.3 Background of the Invention

The background of the invention sets the scene for what comes after. First, it introduces, explains, and defines terms to be used throughout the specification. Second, by discussing patents and/or literature from other sources that could be regarded as relevant to the invention to be disclosed at a later stage, it gives an overview of the

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[21] An Office Action is just a letter sent by the patent office.

state of the art at the time the invention was made. However, this overview is usually written in a somewhat biased manner in that it highlights shortcomings that the invention intends to cure more than other shortcomings, which it may not even mention at all. In doing so, the background of the invention aims at providing the arguments that the invention is indeed novel, non-obvious, and useful.

Although the background of the invention may therefore be slanted toward demonstrating that the invention to be disclosed merits patent protection, it should be honest. It should include all relevant literature the inventor and the agent who has carried out a prior literature search are aware of. It should not misquote or quote out of context. All the bias allows is a certain preference for quotations or arguments in favor of the invention. However, evaluating these literature references requires insight into and experience with the subject matter.

For a patent agent who works in an independent patent office and is therefore less familiar with the subject of the invention than the inventor himself, writing a good background of the invention is very difficult. To be on the safe side and to gain time, agents therefore tend to just quote patent abstracts or claims verbatim and refrain from commenting on the literature they quote. Speculating which theory is a more likely explanation of a set of contradictory observations is beyond them.

In this respect, patent agents working in the patent department of large firms like Procter & Gamble or Unilever have an advantage.[22] They may have started their career within this company in a research department or worked in a plant before switching to patents. They may have direct experience with the subject they describe and thus evaluate the prior art documents themselves. Otherwise, they will know whom to ask within their organization. It is therefore not surprising that some of the best texts I have come across originate from in-house patent departments.

A layperson with a science or engineering degree but who is not a specialist in the field of the invention should be able to understand the text and especially follow its argumentation. Ideally, he should get a feel for the problem the invention aims at solving and appreciate the solution once it has been presented as the invention the specification is all about. After all, that is what the agent filing the application hopes the Examiner will do.

1.2.4 Objects of the Invention

Recent specifications often do not list the objects[23] of the invention under a separate heading. Even so, they will then conclude their background of the invention with what their invention is set to achieve. So a fairly recent patent (Muralidhara et al. 2002) concludes its background to the invention by saying, “Thus, it is either not

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[22] In this context, it is interesting to note that the big three or ABC (Archer-Daniels-Midland, Bunge, and Cargill) rely heavily on outside patent offices.

[23] The word “object” has several meanings. In patent jargon, it means (*Oxford English Dictionary*) “a goal or purpose: the Institute was opened with the object of promoting scientific study.”

possible to produce purified, degummed oil to meet specifications when using frost damaged seeds as feedstock, or it is very cost prohibitive" and then continues with what is, in fact, the object of the invention: "There is a need for a cost-effective process for treating oil extracted from vegetable seeds, especially frost-damaged seeds, to provide a purified, degummed oil having a maximum of 30 ppm chlorophyll-type compounds."

Inventions can have more than one object. A process may aim at a better yield, less effluent, a lower energy consumption, or a lower level of contaminants in the resulting product as in the above example. In fact, it is quite common to list all the advantages of the invention over the prior art. This can then be done, for instance, under the heading *Objects and advantages of the invention,* where the first paragraph is devoted to a general object and the subsequent paragraphs list all the advantages. An example of this approach is given in Adami et al. (2008).

1.2.5 Summary of the Invention

So having set the scene by reviewing the state of the art and highlighting its shortcomings, and by setting some goals for the invention, it is about time to pull the rabbit out of the hat. Accordingly, "It has surprisingly been found that most of the above objects can be attained by …" and then the main claim can be quoted almost verbatim. Patent specifications have indeed something in common with oral presentations: First of all, you tell them what you are going to tell (Summary of the invention), then you tell them (Detailed description of the invention), and finally, you tell them what you have just told them (Claims). In fact, the abstract of the oral presentation as published in the book of abstracts given to all conference delegates on registration fulfils the same role as the abstract on the title page: to whet their appetite so that they come to your presentation or read the specification.

1.2.6 Brief Description of the Drawings

This heading only applies when the specification contains one or more drawings. If it does, their description can be introduced with, for instance, "The present invention is illustrated by the embodiments shown in the appended drawings, in which FIGURE 1 represents …."

I have used this particular phraseology since it provides me with the opportunity to explain the word "embodiment." My *Oxford English Dictionary* describes embodiment as "a tangible or visible form of an idea, quality, or feeling" and illustrates this description with, "She seemed to be a living embodiment of vitality." It is close to but not quite what is meant by "embodiment" in patent jargon. In patents, the word "embodiment" can refer to apparatuses as well as to processes, and a way to define it is a "possible way of realizing the invention." This definition ties in with the lists of embodiments that are quite common in detailed descriptions: “In one embodiment of the apparatus according to the invention. … In another embodiment of the apparatus …. In yet another embodiment …. In a preferred embodiment…,” and so on.

1.2.7 Definition of Terms

In my opinion, far too few patent specifications list definitions of terms, and this is a great pity. With current word processing programs, including them is no problem whatsoever. When you are drafting a text and encounter a term that could be interpreted in different ways, you just define it the way you want it to be defined in the context of the text you are drafting and insert it in the alphabetical list of terms being defined. It has the advantage that you are not fully bound by the way other people have defined that term, and clearly defined terms are a great help in avoiding ambiguities.

If the term “NEUTRALIZATION” has been defined[24] as “the removal of free fatty acids from a crude or degummed oil,” you know that in the patent concerned it can refer to both alkali refining and steam refining. If then STEAM REFINING has been defined as “the neutralization process whereby the free fatty acids are removed by a vacuum stripping process,” you know that the definition also covers the use of nitrogen as stripping medium, despite the fact that the term refers to water vapor.

The definition of terms not only facilitates reading the specification listing these terms. It can also help in putting the specification into its proper context by including a number of commonly used but ill-defined terms. So the terms in Adami et al. (2008) comprise: “TRANSESTERIFICATION is another name for alcoholysis,” and “ALCOHOLYIS is the reaction between an alcohol and a glyceride such as an oil or fat. If the alcohol concerned is methanol, the alcoholysis can also be referred to as ‘methanolysis’ and if it is glycerol, the term ‘glycerolysis’ can be used; alcoholysis is also referred to as ‘transesterification’.”

1.2.8 Detailed Description of the Invention

Now we come to the main course. The detailed description of the invention is the disclosure of the invention for which the applicant wants to obtain patent protection. Accordingly, this description must enable one of ordinary skill in the art[25] to construct

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[24] The examples in this section stem from Adami et al. (2008), an application I drafted myself.

[25] In Dutch, there is the word *vakbroeder*, the literal translation of which is “brother in the profession.” I like this word and regret that there is no similarly illustrative English equivalent.

the apparatus according to the invention or carry out the process according to same.[26] Consequently, the description must discuss all aspects the inventor regards as essential to his invention. Failing to do so can lead to a successful opposition on the grounds of "insufficient disclosure"; this happened recently to a patent (Sampalis 2004) on the krill flavonoid known as lucenin-2 that was granted to Neptune Technologies & Bioressources[27] and that was subsequently opposed by Enzymatic Ltd. and Aker Biomarine ASA.

Another reason why it must do so is that the detailed description of the invention is also the basis for the claims. So if a claim specifies that the process be preferably carried out between 40°C and 80°C, the process instructions in the detailed description must quote these very same figures; this is the reason why reading a detailed description can be somewhat tedious. Hopefully, it becomes less so when the reader has developed a feeling for what he can skip and why.

Developing this feeling requires some insight into why claims tend to be formulated the way they are. I will discuss claims in more detail under their own heading, but I want to point out at this stage that the set of claims at the end of the specification defines the scope of the invention. If the validity of a patent is disputed, it is not the patent as a whole that is at stake but only its individual claims. Consequently, claims tend to be formulated in such a way that they provide fallback positions. If a broad claim is found to be unacceptable, the list of claims should include a different, less broad claim that hopefully turns out to be acceptable.

Let me illustrate this crucial point with an example. Say you want to protect a process involving a reaction between two chemical compounds A and B. Your first or main claim could claim just that, "A process to produce something useful or other, characterized in that compound A is allowed to react with an aqueous solution of compound B." Such a claim would give very wide protection, but can you be really sure that nobody ever reported this reaction? If somebody had and this claim was your only protection, you would lose it. Therefore, you narrow the field of protection with narrower and narrower claims.

One way of narrowing might be by specifying the reaction temperature. So you formulate a claim that depends on the main claim, which only specifies that A is allowed to react with B, by adding a temperature limitation: Process according to claim 1 in which the reaction temperature is maintained between 0°C and 100°C. Since compound B is dissolved in water, this is not much of a limitation: below 0°C, the solution of B in water would freeze, and above 100°C, it would evaporate. However, if somebody were to oppose this dependent claim, he should not only demonstrate that the prior art discloses that compound A has already been allowed to react with an aqueous solution of compound B, but he should also demonstrate that in the prior art, this reaction was carried out within the specified temperature range of 0–100°C.

Let us assume that the prior art document mentioned nowhere that the reagents were cooled or heated. Then it could be argued that the prior art reaction was carried

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[26] Yet another example of legalistic patent jargon. Why not "carry out the invented process"?

[27] This is not a typing error for Bioresources; I checked it on the Internet.

out at ambient temperature. In that case, a reaction that is specifically carried out between 0°C and 100°C is still anticipated by this prior art document. However, if the claim specifying the temperature range were to be followed by subsequent claims specifying ever more narrow temperature ranges, one or more of these subsequent claims will no longer be anticipated by this prior art document, and that is where all these preferences come in.

So the detailed description of the invention starts by stating that the reaction can be carried out between 0°C and 100°C. Then it states that preferably, the reaction is carried out between, say, 30°C and 90°C, and more preferably between 40°C and 80°C. These figures have little technical value. They are there for patenting reasons. They provide fallback positions in case the broader claim, from which the narrower claims specifying these ranges depend, is found to be invalid. Since claims are based on the detailed description, the detailed description must contain all the fallback positions that are reiterated in the claims.

For a number of reasons, not everything mentioned in the detailed description of the invention has to lead to a claim. One reason for mentioning something is to ensure publication and thereby prevent other people from claiming it as an improvement over what else you describe and claim. Another reason can be that without it being mentioned, a reader would not be able to replicate the invention. Yet another reason for not claiming something is that the claim would not provide any further protection. Finally, it might be difficult to detect the claim being infringed, so why bother claiming it?

So in the detailed description of the invention, the inventor discloses in detail how to make his invention work and highlights critical and non-critical aspects. When he carries out a reaction, he will tell what reagents to use. If, for instance, one of these reagents is an alcohol, the inventor will tell which alcohol to use. If there are only a few alcohols that work, he may formulate this as, "an alcohol selected from the group consisting of A, B, C, and D." This is patent jargon for just "A, B, C, or D," which means the same. Does this way of formulating include alcohol mixtures? I think not since mixtures are often mentioned as well: "an alcohol selected from the group consisting of A, B, C, D and their mixtures," which could be phrased more simply as, "A, B, C, and/or D."

The question of whether or not a certain way of formulating includes or excludes a possible interpretation can often be vital. If the interpretation is excluded, it means that this interpretation is likely to fall outside the claims and thus provides a way to circumvent[28] the patent. Consequently, the detailed description goes to great lengths in being safe rather than sorry. Saying "absolute alcohol" may be open to interpretation, so it goes on to define that this absolute alcohol must contain less than 0.1 wt% water, and preferably less than 0.01 wt% water. So if a claim mentions "absolute

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[28] The *Oxford English Dictionary* mentions an archaic meaning of "to circumvent": "to deceive, outwit," meanings that are highly appropriate in the present context. The Dutch, being seafarers, use the word *omzeilen,* which means "to sail around."

alcohol," the reader can find out what this means by going back to the detailed description of the invention.

In general, the detailed description of the invention follows the process step by step, which is quite logical. So it starts by describing the raw materials. If one of these is an edible oil, this has to be defined. Is it an animal oil or a vegetable oil? Does it include single-cell oils? Or does it not matter? In that case, the description "triglyceride oil" might be preferable, but then is it a crude[29] oil or has it already been water degummed? Or is there just a preference for water degummed oil? All these kinds of things will be found in the detailed description and allow the reader to move on quickly and read somewhat diagonally. They are just there to prevent the patent from being circumvented. That also holds for remarks that some description or other "does not limit the scope of the invention" or that "further embodiments will occur to those skilled in the art."

To avoid having to go into even further detail, the detailed description of the invention may incorporate some shortcuts such as, "as is known to those skilled in the art." It can also refer to other documents such as Official Analytical Methods, literature articles, or even "my co-pending application," which can then be included by reference.

1.2.9 Examples

Patents dealing with an apparatus often do not illustrate the invention with one or more examples but use the drawings for this purpose. Process patents, on the other hand, nearly always include examples. Since most industrial processes started their life in the laboratory, the examples may well describe laboratory experiments. The description should be sufficiently detailed to enable the reader (who can be supposed to be skilled in the art) to repeat the experiment. So if a special piece of equipment was used that is considered to be critical, its supplier and type have to be mentioned.

On the other hand, there is no need to mention suppliers of common laboratory chemicals, as scientific journals tend to do. Uncommon chemicals should be specified, as has been done in a patent describing a hydrogen sensor (Example I in Hoffheins and Lauf 1995): "First the interconnections **21** were applied using DuPont 6120 composition …." This tells you where to buy it and what to order.

Most processes involve a range of process variables and the examples can be used to illustrate their effects. Accordingly, the example text may start with a kind of introduction informing the reader what the example will illustrate. At the end, the text may conclude that this example clearly illustrates how wonderful the invention is. So the example not only illustrates but also provides supporting evidence. Patents that have been drafted in Japan often start with a comparative example, a kind of

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[29] Specifications that have been translated into English regularly refer to "crude oil" as "raw oil" (*Rohöl*).

reference, that is considered to be representative of the prior art, and then use its results as a baseline.

Examples can also serve as the basis for claiming a whole range of compounds, such as, for instance, "monohydric alcohols with up to six carbon atoms." This definition includes methanol but also tertiary butanol and hexanol, which are rather different compounds with different boiling points and different reactivities. If the examples only used methanol, it could be argued that the range of monohydric alcohols claimed was too wide to be true. By illustrating the invention with examples that use different alcohols,[30] claiming a range of compounds is considered to be justified even when some of the compounds included in the range may hardly work when tested. They may also be much more expensive and therefore be useless, but again, this lack of usefulness does not prevent the patent from being granted.

The evidence presented by the samples can be more or less shaky. There is nothing wrong with using a well-known piece of measuring equipment, but what about taste panels? I know they are used and play an essential role in the food industry, but I regard their evidence in patent examples as dubious and too prone to manipulation for my liking. After all, the Examiner will not question the experimental data; they are supposed to be a fair representation of what happened.

Personally, I find patent examples can be a source of inspiration and I therefore recommend reading them with an open mind. Patents are filed by people from all over the world with all kinds of different approaches, and their ways of tackling a problem may well be different from what you are used to; they may even be better.

1.2.10 Claims

In Dutch, patent claims are called "conclusions" and old French patents list them under the heading "summary" (résumé). They represent the gist of the patent, and for that reason, the Examiner limits his comments on a patent application primarily to the validity (or the lack thereof) of the claims. If some passages in the specification are deemed to be insufficiently clear, he may also point this out and suggest amendment. So in his Office Action,[31] he states which claims he accepts and which he rejects. Then the applicant can argue that rejected claims should be admitted and/or submit new claims and argue that these meet the objections given in the Office Action. Similarly, opposition to a granted patent or a court case asking a granted patent to be declared invalid is limited to the claims of the patent concerned.

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[30] When claiming monohydric alcohols with up to six carbon atoms, it is not necessary to include examples with a whole range of different alcohols with up to six carbon atoms. If the examples include the use of two alcohols, such as methanol and ethanol, it is considered to be a sufficient base to claim the whole range.

[31] Correspondence originating from a national patent office is referred to as Office Action.

However, as will be explained in more detail later, there is a fundamental difference between opposing a patent before the Opposition Division of a patent office and challenging it in court. If the Opposition Division concludes that a claim as granted is invalid, the patent owner (assignee) can suggest a new claim and argue that this new claim should replace the old one. The opposition is thus an extension of the examination. In court, claims can only be revoked; they cannot be amended or replaced. This difference has to be taken into account when deciding how to attack a patent that has been granted to a competitor. If you have valid arguments against one or all claims, but the specification supports[32] amendments that would make them acceptable, going to court may be advisable. In Europe this has the disadvantage of having to sue the competitor in each country where he has obtained a patent.

As is only to be expected, the inventor and/or patent owner wants his claims to cover as wide a field as possible. For that reason, the list of claims is often preceded by a paragraph pointing out that the detailed description and the examples are illustrative only. I regularly used the following disclaimer until an Examiner objected:

> The invention, therefore, is well adapted to carry out the objects and attain the ends and advantages mentioned, as well as others inherent therein. While the invention has been depicted, described, and defined by reference to exemplary embodiments of the invention, such references do not imply a limitation on the invention, and no such limitation is to be inferred. The invention is capable of considerable modification, alteration, and equivalence in form and function, as will occur to those ordinarily skilled in the pertinent arts and having the benefit of this disclosure. The depicted and described embodiments of the invention are exemplary only, and are not exhaustive of the scope of the invention. It is intended that all such variations within the scope of the invention, giving full cognizance to equivalence in all respects, be included within the scope of the appended claims.

However, the present section is not about legalities but about reading a patent and its claims. How does one read a patent claim? First of all, we should make a distinction between independent claims and claims that depend upon one or more claims listed earlier (Bloomer 2004g). The first claim (claim 1) is always an independent claim. It is likely to start with the words "A process" or "An apparatus" followed by a short description of what the process or apparatus is used for or can achieve. For example (Muralidhara et al. 2002), "A process which is effective for providing a decolorized and degummed oil having less than about 50 ppm phosphorus and less than about 5 ppm chlorophyll-type compounds from vegetable oil, the process comprising …." These and similar descriptions do not limit the scope of the invention. If you perform the actions listed by this claim and the resulting oil contains more than 50 ppm phosphorus and/or more than 5 ppm chlorophyll-like compounds, you are still infringing.[33] Similarly, if a claim starts with, "A confectionery fat made by

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[32] This "supports" is jargon again. It means that the specification must provide a basis for the amendment. Say the claim being disputed mentions a periodical movement and the prior art used to dispute this claim refers to a vertical movement; then an amendment could only limit the claim to a horizontal movement if the specification explicitly mentions this horizontal movement.

[33] My reviewer is not too certain about this. I would not be surprised if this statement was not valid in all countries.

interesterifying …," and you make such a fat by interesterifying the fats listed in the claim, and the interesterification product meets whatever further requirements are listed but you do not use it in confectionery but as a margarine hardstock, it is still an infringement because the word "confectionery" is only illustrative.

Then the main claim can continue in one of two ways. One is to simply list the features of the invention: "A process comprising features A, B, and C." The other way is to start with a preamble that lists features of the prior art that are also part of the invention. The preamble is then followed by the so-called transitional phrase (*characterized in that* or *in which*,[34] etc.) that introduces the so-called body of the claim that describes or lists the inventive features and defines in what respects the invention differs from the prior art.

An example of a quite extensive preamble is given by Kogan and Pelloso (1982):[35] "A process for rapidly increasing the solids content in a triglyceride oil containing a high level of polyunsaturates and a low level of saturated fatty acids which comprises subjecting a liquid triglyceride oil to interesterification at a temperature between a few degrees Celsius below the initial cloud point of the oil and a few degrees Celsius above that cloud point in the presence of a low-temperature active catalyst, continuing the interesterification for a period of time effective to increase the quantity of triglycerides which solidify at the initial cloud point, cooling the triglyceride oil to below its initial cloud point to form a liquid fraction and a solid fraction, characterized by …." This preamble describes the Vandemoortele directed interesterification process, and what comes after is the Nabisco Brands contribution.

When using a preamble, the only prior art features listed should be those that are essential for the process or apparatus to work, because including non-essential features just limits the scope of the invention. In principle, the list could be limited to those features that are modified by the invention so that the subsequent body of the claim can then refer to "said this" and "said that." As always, limiting the number of features in a claim has the danger that unsuspected prior art turns up, so including features that form an almost integral part of the process or apparatus being claimed hardly limits the scope of protection but does reduce this danger.

If no preamble is used, the claim just lists the features that form part of the invention: "A process comprising …" and then a list. Again, the list tends to be limited to as few features as possible with additional features being introduced by subsequent claims. So if claim 1, the main and independent claim, reads: "A process comprising

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[34] To highlight the transitional phrase, Dutch application publications, which were distributed as stencils, used to extend it by inserting spaces in between the letters "m e t h e t k e n m e r k d a t" (characterized in that). This could be done with an ordinary typewriter as used to make the stencils.

[35] Nabisco Brands, a merger between Standard Brands (margarine) and Nabisco (biscuits), was discussing a license with the Vandemoortele Group for the directed interesterification process of the latter (De Lathauwer et al. 1981). This patent by Nabisco Brands was an attempt to strengthen its negotiation position.

feature A", the next claim (claim 2), could read, "The[36] process according to claim 1, further comprising feature B" or "The process according to claim 1, characterized in that it further comprises feature B." Claim 3 could then introduce additional feature C, etc. Writing dependent claims like this is a kind of shorthand that saves a lot of space and highlights what is different at the same time.

However, with respect to dependent claims, there is a fundamental difference between US practice and European practice. In the US, a claim may not depend on preceding claims that depend on more than one claim themselves, whereas in Europe, this limitation does not exist. In Europe, claim 2 might read, "The process according to claim 1, in which …"; claim 3 might read, "The process according to claims 1 or 2, in which …"; and claim 4 might read, "The process according to any of claims 1 to 3, in which …." The US would allow claim 2 as indicated above; claim 3 as formulated above would also be allowed since it only refers to claims that depend upon single claims; but claim 4 as formulated above would not be allowed in the US.

This difference causes equivalent patents (patents belonging to the same family) to list more claims in the US than in Europe, where the EPO charges an additional fee for the 16th and each subsequent claim.[37] In Europe, it pays not to have too many claims.

The use of multi-dependent claims forces the reader to track what is claimed. The main claim may stipulate feature A, and dependent claim 2 may stipulate feature B. If then claim 3 depends on any previous claim and stipulates feature C, the embodiments covered so far are A (claim 1), A + B (claim 2), A + C (because claim 3 depends on claim 1), A + B + C (because claim 3 depends on claim 2). When more and more claims start depending on each other, the situation may start to look rather complicated, but in practice, it is not that bad. Just assume that all features accumulate and pay special attention to those claims that do not depend on all previous claims. Ask yourself why their dependence was limited; often, the answer turns out to be quite logical. The esp@ce website now also provides "trees" that show how claims depend on each other, but I have only discovered this recently and cannot report any experience with this feature.

At first sight, some claims may look superfluous. Take, for instance, the following two consecutive claims in the same patent, the main claim of which comprises step a):

The process according to claim 1 in which water is added during step a).
The process according to claim 1 in which no water is added during step a).

Why bother spelling it out when, apparently, the process works with and without the addition of water? There are two reasons for this. Just imagine that the Examiner or somebody opposing the patent finds a publication that describes the

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[36] Independent claims start with "A process" or "An apparatus"; dependent claims start with, "The process according to" or "The apparatus according to."

[37] Up until April 2008, this additional fee applied to the 11th and each subsequent claim.

process as disclosed in the main claim of this patent. That would constitute prior art and invalidate this main claim. Imagine as well that this prior art publication describes a process that includes the addition of water during step a). Then this prior art also invalidates the first of the two claims listed above, but incorporating the second of these two claims into the main claim results in a new main claim that is novel with respect to the prior art document that described the process with the addition of water. Therefore, this new main claim will be allowed, whereas no claims would be allowed if the two "contradictory" claims had not been included in the first place.

Actually, the above example also illustrates another consequence of allowing claims to be multi-dependent. Their subsequent dependent claims are more likely to be allowed if they also depend on the two "contradictory" claims than when they only depended on the main claim. But, as usual, the coin has two sides. A dependent claim that depends on multi-dependent claims covers a wider field and therefore runs a higher risk of facing prior art than a more restricted claim. In practice, this amounts to another factor to be taken into account when writing claims and especially how they depend on each other.

The second reason to include these two claims is that it prevents the competition from claiming one of them in its own name. Let's assume that company A (Applicant) files a patent application that does not include the two claims listed above. No prior art emerges and so a patent is granted. Company C (Competitor) does not like this at all and therefore files an application itself by "disclosing" an improvement of the process disclosed by company A. If none of the examples in the patent granted to company A describes the addition of water and the specification does not mention the addition of water either, company C now states: "Surprisingly, it has been found that the addition of water has all kinds of unexpected advantages." Company C then files a patent application with a main claim that describes the process of company A as the preamble to its main claim that is further characterized by the addition of water during step a). This addition is novel and apparently offers all kinds of advantages, and so company C obtains a patent.

However, company A can prevent company C from operating its process since this would infringe on the patent held by company A. On the other hand, company A is not allowed to profit from the improvements, real or otherwise, that have been introduced by its competitor because this competitor (company C) has obtained a patent protecting these improvements. Stalemate. So they have to talk to each other and if one of the companies does not want to talk, the other one can go to court and ask the judge to rule that a license be granted. The judge may well think this is a reasonable request and rule that both companies allow each other to use each other's process.[38] So not listing the two claims finally led to company A allowing its competitor to operate its process, which is exactly the opposite of what company A set out to do when applying for patent protection.

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[38] This is referred to as "cross licensing."

1.3 Obtaining a Patent

Apparently, some inventors or their agents still believe that obtaining a patent requires divine intervention.[39] Henson et al.(US Patent No. 6,554,117, issue date 29 April 2003) introduce their claims as follows: "Having disclosed the invention as required by Title 35 of the United States Code, Applicants now pray respectfully that Letters Patent be granted for their invention in accordance with the scope of the claims appended hereto. What is claimed is: …." As will be shown below, just praying is an oversimplification of the granting procedure.

Before discussing how to obtain a patent, I want to devote a few words to the two options of trying to obtain a patent or keeping the invention secret. Don't forget that filing an application causes it to be published. If it does not lead to a granted patent, this means that you have paid money to betray your secrets. Which alternative to choose depends on a large number of factors and I will only discuss a few. If your invention reveals itself when you sell it (yet another mousetrap or nutcracker), you cannot keep it secret and infringement is also immediately obvious. In that instance, seeking patent protection is advisable. At the other extreme are process improvements that are not apparent from the resulting product, nor by the purchase of different ingredients, so that detecting infringement is almost impossible. In that case, keeping the invention a secret may well be the best alternative, also because the competition is unlikely to deduce what you are doing by reverse engineering.

However, keeping things secret entails the risk that somebody else gets a patent in his name for what you do, and that would be most annoying indeed since that patent would make you infringe on your own invention and prevent you from doing what you have been doing for years. To protect you from ending up in a situation like that, you can try to rely upon "prior use." In Belgium, for instance, you can deposit a document with a notary public that describes what you do. If you then face an infringement action, you can claim prior use if this document was deposited before the priority date of the patent you are accused of infringing. However, this prior use only entitles you to continue doing what you described. If there have been improvements you did not describe, you may not use them, and if you increased the capacity of your plant since you deposited your description, the prior use limits you to the scale you described. I fear that in practice, this prior use is pretty useless and I have regularly advised clients against relying on it. In fact, the risk that somebody else obtains a patent for what you are doing and want to continue doing is a very strong and often compelling reason to apply for a patent yourself.

It tells your competitor what you are allowed to do and may prevent him from having an authorized look at what you are doing. I am referring here to what is called a *beschrijvend beslag* in Dutch and a "descriptive seizure order" or "Anton

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[39] I went to www.google.com/patents and searched for "pray" AND "granted" and this yielded 144 hits.

Piller order" in English. In Belgium or France, for that matter,[40] a patent holder suspecting infringement can go to a judge and ask for an inspection of the plant to describe the alleged counterfeited process. He can then use the report when prosecuting for infringement. Often though, the judge allows such an inspection without having a clue what it is all about and then sanctions industrial espionage. So the first thing the reluctant host of the inspection does is sue his visitor for obtaining trade secrets in a most unlawful manner,

Because patents are national affairs, books on patents tend to be rather parochial. When discussing whether to apply for a patent or keep the invention secret, they hardly point out that if you opt for secrecy, this secrecy is worldwide. Opting for patent protection, on the other hand, only concerns those countries where you decided to file an application and a patent is granted. The rest of the world can freely make use of your invention, which you so kindly allowed to be published.

On the other hand, allowing it to be published can also be regarded as publicity. "Beware, I am working in this field and even if this Application Publication does not lead to a granted patent, there may be more in the pipeline that will." If you were a customer, which supplier would you prefer: the one who made the invention and continued to work in the field or the copycat who hopes to make a quick buck?

Whether to file and where, or whether to file provisionally (Bloomer 2004b), are management decisions that not only have financial consequences but also affect the steps to be taken by the patent agent. Say a US company wants to protect its invention in Germany because that is where its main competitor operates; it can file a German application, or it can file a European application and designate Germany. Filing in Germany means that the US application must be translated into German before it can be filed, whereas for a European application, the US text does not have to be translated. That will only become necessary when the European patent has been granted and enters the national phase.

On the other hand, it costs more to apply for a European patent designating a single country than it does to apply directly in that one country. If you want to apply in four countries, the European route is cheaper but has the disadvantage that you put all your eggs in one basket. If no European patent is granted, you have no protection, whereas if you had applied in several countries, there is a possibility that one of them may grant a patent.

When making such decisions, management should consult a patent agent since he can give a rough estimate of the costs involved in the various options and he can also give an opinion on the likelihood that the intended application will lead to a granted patent. To arrive at this opinion, he may have to carry out a literature search, but preferably, the inventor will have done this already so that the agent will only have to study the literature provided by the inventor.

It may sound rather obvious, but the first thing you need when you want to obtain a patent is an invention. At one stage, one of my clients told me he wanted patent protection for something he intended to do and asked me to draft a patent. So I asked

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[40] A large proportion of Belgian law is a straight copy from French law.

him what the invention was all about or, in other words, at what stage I could write that “Surprisingly, we found ….” This question resulted in an awkward silence since what he intended to do was pretty straightforward.

Even so, what does not appear to be an invention can sometimes be dressed up to look like one. Unilever has been instrumental in developing pulse-NMR for measuring the solid fat content (SFC) of partially crystallized fats. Its cooperation with Bruker Optics led to the Minispec, which became generally available for SFC measurement for quality control and product development. Soon after, Unilever patents started to describe fat blends in terms of SFC parameters by introducing N_{10}, N_{15}, and N_{20} values, which are the SFC data obtained at 10°C, 15°C, and 20°C, respectively.

Describing blends in this novel way made them look novel, and blends that had been made in the past and might well constitute prior art could now be described by quoting their SFC values and presented in such a way that early publications could no longer be quoted as prior art since they lacked these SFC data.

Say an early publication defines a fat blend by giving composition ranges of the blend components: “A fat blend consisting of 20–60% component A, 15–45% component B, and 40–55% component C.” If then a later applications claims, “A fat blend consisting of components A, B, and C, characterized in that the N_{10} value is within the range of …,” it is not immediately clear that the early publication might destroy the novelty of the fat blend in the application. On the face of it, it does not and so the Examiner is likely to accept the blend in the application as novel. It is only during an opposition that the opponent can provide experimental evidence to demonstrate prior art by preparing a blend that meets the requirements of the early publication, measuring its SFC profile, and then showing that its SFC values fall within the ranges specified in what had then become a patent.

I must confess that I did something similarly devious myself. When developing the Total Degumming Process (TOP), I realized that a fine dispersion of the degumming acid in the oil was crucial, but so had Mag and Reid (1980). They specified that “the acid is dispersed throughout the oil in the form of droplets smaller than about 10 micron in diameter.” How could I present TOP as novel with respect to this earlier publication? I did this by buying a Centrifugal Automatic Particle Analyzer (Horiba CAPA 500) and describing the dispersion in a novel way (Dijkstra and Van Opstal 1987): “… whereby the degree of dispersion is at least such that at least 10 million droplets aqueous acid per gram of oil are present, forming an interface between the acid droplets and the oil of at least 0.2 m^2 per 100 g of oil.” Since both dispersions led to a fast reaction between the degumming acid and the non-hydratable phosphatides, they may well have been about equally fine, but from the way they have been defined, this does not follow, and so the early document could not be considered as prior art.[41]

What happens when the patent agent thinks that the process or apparatus being considered for patent protection is an invention and management opts for patent

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[41] Even so, I approached Canada Packers and arranged with Mr. Mag that this company would give a license to Vandemoortele if a Canadian or US company wanted a TOP license.

protection? The first thing to be done is to decide where to file the priority application because under the Paris Convention, it is not necessary to file applications immediately in all the countries where patent protection will eventually be sought.

This convention gives you a year to make up your mind whether or not to proceed. If you file the priority document in the UK, you can ask for a literature Search Report[42] and use this when making up your mind. If you intended to file in several countries but then decide not to pursue the application, having been able to postpone all applications except the priority one has saved you money since in addition to translation costs, there is also a fee for filing each patent application.

In the US, there is the possibility of filing a provisional application that may offer advantages, and there are the Patent Cooperation Treaty, the European Patent Office, and many more possibilities. I am not going to discuss them but just want to point out their existence and that this is the point in time when the patent agent should advise which course to follow and why.

When it is clear where the priority document will be filed, the next thing to be done is drafting a specification. This requires cooperation between the inventor and the patent agent. This cooperation can be quite stimulating to both parties provided they respect each other's expertise and are willing to listen and learn.[43]

From bitter experience I also know that such cooperation can be utterly frustrating. One of my clients asked me to draft a specification and I started with the innocuous words, "Vegetable oils as obtained by expelling and/or extraction require extensive purification." I sent my draft to my client's patent agent and asked him to take care of the legal aspects. Instead he changed my "and/or" to "and." So I explained that cocoa butter and virgin olive oil are obtained by expelling, that soybean oil is obtained by extraction, and that canola oil is obtained by expelling the seeds and then extracting the expeller cake. Instead of concentrating on the legal aspects, this agent had completely rewritten my draft and converted it into technical nonsense. It took me a long time to spot all the changes since he had not used the *Track Changes* subroutine, and then I had to explain to my client why my invoice exceeded expectations.

Fortunately, I have also worked with patent agents who asked me to provide them with background information and explain what I had written and then suggested another and often better way of expressing what I had wanted to convey. After having gone through my draft in such a manner, we both felt we had learned a lot, had come to appreciate each other's contributions, and had arrived at a much improved text and earned what we were going to charge my client.

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[42] The fee of £ 150 is well worth it and much lower than the few thousand dollars mentioned in Bloomer (2004c).

[43] Patent agents working in an outside office may not necessarily be conversant with the jargon used in discussing edible oils and fats. I remember one patent agent who preferred to speak of removing gums by filtration rather than by centrifuge. He had not realized that "our" gums are rather viscous fluids. Instead, he interpreted the word "gums" as referring to something that had more the consistency of jelly babies.

Such an appreciation requires a certain insight into what the other party is doing. I hope that by providing my readers with some background on how to obtain a patent, this will help them to cooperate with patent agents in a mutually stimulating manner. In fact, working together may be so stimulating that it causes the invention to increase in scope. The inventor may become aware of aspects he had not thought of before; the agent may ask the inventor if his invention might work in other fields; they may think of additional advantages, and so on – a real brainstorming session, in fact!

Often inventions have more than one inventor. Then it is advisable to ask most, if not all, of them to attend the meeting with the patent agent where he is instructed about the invention or where the draft application will be discussed. Inviting a specialist who has not previously been directly involved in the invention can be a good thing, but make sure that non-technical managers do not attend such meetings. When inventors discuss their invention with a patent agent – and who does not like discussing his achievements? – the invention may develop and grow as a result of this discussion. In my experience, people attending such meetings may not remember afterward who made which contribution. On paper, this might cause problems with US applications since US patent law is very strict on who can and must be listed as inventor (Bloomer 2003). But, as we say in Dutch, "The soup is not eaten at the same temperature as it is served."[44]

In general, it is up to the inventors to provide the background knowledge and a list of possibly pertinent prior art documents. Preferably, they will also comment on these documents by telling the person who will draft the application (henceforth to be referred to as the "writer") what they dislike about them and/or in what way their invention is better or can be made to look better. This enables the writer to build his case and introduce arguments in favor of the invention. These arguments may be phony. The writer may denounce a prior art process by saying that it uses solvents, while he may have advocated the use of the very same solvents a few days earlier in a different application.

The inventors always provide the factual data to be incorporated in the Examples. This may be in the form of one or more laboratory reports or internal reports on a plant trial. However, the patent agent may well ask for certain additional experiments to be carried out to illustrate certain aspects of the invention. Such instances ask for a discussion between the inventor and the patent agent to make sure that the experiments are not unduly complicated but still provide the answers required.

It is imperative that one or more inventors read and approve the final draft of the application before it is filed and preferably take their time over it. I know it is difficult, but they should preferably study the final draft with a fresh mind, as if they saw the application for the first time. In addition, they should also verify the way the process conditions have been quantified in statements such as "less than K%, preferably less than L%, and more preferably less than M%." After all, they are the experts with respect to the technology involved in the invention. By the time the inventors

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[44] There is no equivalent proverb in English, but the Dutch one means that in practice, rules are often applied less strictly.

go through the final draft, they should be sufficiently aware of patenting aspects not to balk at such statements full of patent jargon.

It is up to the patent agent to make sure that, in his opinion, the final draft meets all legal requirements and provides the protection his client has asked for. He may suggest that perhaps the scope of protection could be enlarged and that what started as an application claiming an apparatus could also claim the process carried out in that apparatus, or vice versa, but on the whole, he should respect what is customary in the trade. An equipment manufacturer supplying refiners is unlikely to sue his customers because they operate a refining process that has been claimed in a patent that also claimed that apparatus. He is much more likely to consider suing the manufacturer of that apparatus since that manufacturer is his real competitor.

Care has to be taken when enlarging the scope of protection by including apparatus claims in a process patent; it could turn out to be most embarrassing if the apparatus turns out to have been used in an entirely different process and was therefore known per se. Then the Examiner may argue that using the known apparatus for a different process is hardly inventive. This means that you have to counter-argue that comparing these processes is like comparing apples with pears, that what holds for one process does not necessarily hold for another process. You may have to identify documents that stress the importance of certain aspects for one of the processes and conclude that these are unimportant for the other process. All this can lead to lengthy and therefore costly correspondence with an uncertain outcome. It is much better to decide beforehand that enlarging the scope of the invention is hardly worthwhile in this case.[45] Why protect a piece of equipment that might also be used in the sugar industry when your only customers are edible oil refiners and protecting an edible oil process provides you with all the protection you want?

It is also up to the patent agent[46] to provide all the forms to be filled in and signed by the inventors and/or the applicant(s) and to make sure that whatever fees have to be paid are paid and that all legalities are taken care of (Bloomer 2004d). That is the service his firm, the patent office, provides and for which it charges a fee.[47] It is up to this office to keep track of all the legal changes in this red tape and inform its clients, who have instructed this office to pursue their applications and look after their patents of such changes. This office must also warn its clients when annuities are due and make these payments once their clients have instructed them to do so.

So after the priority application has been duly filed, its receipt will be acknowledged by the patent office in the form of an application number to be used in all future correspondence. Thereafter you have to wait for the Search Report or any Office Action asking for clarification, most of which are of a legal nature and are dealt with by the patent agent's office.

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[45] The German language has a delightful expression: *In der Beschränkung zeigt sich der Meister,* which, for lack of an equivalent, I can translate as "Restraint reveals the hand of the master."

[46] Does this remind you of patent specifications? "It is a further object of the invention …."

[47] In Dutch, this fee is called an "honorarium." Never refer to the invoice sent by such exalted persons as patent agents as a bill or check, but only as a monetary gift in honor of their profession.

The next time the inventor becomes involved in the application procedure is when the patent agent receives the Search Report. In this report, the Examiner lists documents he considers to be pertinent and in the Extended Search Report, he also comments on the application. Then it is up to the inventor or one of his colleagues who is fully familiar with the subject matter of the invention to ascertain that in his opinion the Examiner has correctly understood what the invention is all about. If he comes to the conclusion that there is some misunderstanding, it could be very helpful if he can also point out where this misunderstanding originated.

Examiners work their way through many applications and ensuing correspondence. As a rule, they have become specialized in certain fields, but even so, they may not immediately understand how the invention for which an application has been filed differs from what is generally known. After all, they face a long backlog of work and try to spend a minimum of time on each job at hand.

The reason that I recommend that the inventor has a look at the arguments put forward by the Examiner is that patent agents tend to react to those arguments by concentrating on their legal aspects. Someone familiar with the subject can detect flaws and explain them in technical terms. Patent agents are less familiar with the technical aspects and therefore tend to accept the arguments made by the Examiner and find a way around them in legal terms. They also prefer a more tactful approach in dealing with the Examiner; telling him that he has not understood things properly is not exactly in line with this approach. In fact, "All correspondence with the patent office must be carried out with decorum and courtesy" (Bloomer 2004e). Even so, the strongest case results from combining the technical arguments with the legal arguments,[48] which means that the patent agent should provide the inventor with an opportunity to comment.

Accordingly, when the Examiner argues a lack of novelty, it is up to the inventor to detect essential differences between his invention and the prior art quoted against it. On the face of it, this prior art document may indeed look like the most perfect document you can wish for when opposing a patent, but there may be subtle and essential differences. Say the prior art process starts with a crude oil but does not specify whether this oil has been water degummed or not, while the invention starts specifically with water degummed oil and both processes are quite similar. By reading that the examples of the prior art document start with soybean oil with phosphorus contents of 650–920 ppm P, the inventor can convincingly argue that the prior art document only dealt with oil that had not yet been water degummed. He may also provide a technical argument that shows that the presence or absence of hydratable phosphatides affects the process. Having been provided with this background information and argument, it is up to the patent agent to present them in the proper manner by referring to the appropriate paragraphs and sections of the Patent Law.

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[48] In the US, the patent agent may lard his reply to the Office Action with phrases like, "See *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977). Also MPEP 2144.05 II B," which no doubt make sense to insiders and may strengthen his arguments but do not mean anything to a chemist.

Say the Examiner argues that he considers the invention to be obvious. Then the inventor is best placed to come up with recent literature that teaches away from what the Examiner felt was obvious. Whether an invention is obvious or not is always rather subjective, but if several experts or handbooks teach one way and the prior art document goes the other way, people tend to go along with the experts. There is, of course, the possibility that the prior art document demonstrates why the experts are wrong, but going so deeply into the basics of the matter is beyond the scope of most correspondence between the applicant and the Examiner. Keep it simple, and hopefully, the Examiner will agree. As mentioned before, Examiners are busy people.

On the whole, patent agents know when to contact the inventor or the assignee. They may do this to get technical feedback, to get further instructions, and above all, to get money. They may also do this to inform the applicant of a "notice of allowance," which means that the Examiner has decided that a patent be granted.

In the US, this notice is final. In Europe, on the other hand, the granted patent, which will be published as a B1 document, has a little notice at the bottom of the front page:

> Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European Patent Convention).

So whereas in the US, you have to go to court to argue that a patent should not have been granted, the European Patent Office has an internal Opposition Division that will consider new evidence or arguments. Accordingly, a Notice of Opposition should list this new evidence and provide arguments why one or more claims should be revoked. The opposition procedure starts with an exchange of documents between the parties, each of whom can also ask for a hearing (oral proceedings) before the Opposition Division. Each party can also appeal against the decision of this Division.

Because the application is published before the granted patent is published, potential opponents know what patent may be in the pipeline and may decide to act early by sending a letter to the EPO informing the Examiner about prior art they are aware of but that has not been published in the literature Search Report. This is the "poor man's opposition" since it does not require any opposition fees to be paid. It has the disadvantage that the patent that is eventually granted will then have taken this prior art into account and include new claims that can no longer be opposed on the grounds of that particular prior art.

After a European patent has been granted, opposing the granted patent can lead to one of three outcomes. The patent may be maintained, it may be amended, or it may be revoked in its entirety. If it is maintained, this means that the arguments in the opposition were insufficiently strong. If they were considered to be sufficiently strong, the patent is revoked in its entirety. The awkward case is when the patent is amended, when the Opposition Division is of the opinion that the patent still contains some patentable material, and it is anybody's guess where the Division will draw the line. Accordingly, a company that does not like a patent that has been granted to its competitor and that can choose between opposing this patent at the

EPO and going to court may well prefer going to court since the court cannot amend claims but only revoke them. By not opposing the patent through the EPO but going to court instead, the company will ensure that any remaining claims are left as they are and without amendments. On the other hand, if this company has grounds that should cause the patent to be revoked, it should oppose. So if the main claim as granted extends, for instance, beyond what had been claimed in the application, it provides a clear case for opposition and revocation of the patent. If the case is less clear, opposing may well be a case of "Whoso diggeth a pit shall fall therein."

Applying for and opposing a patent implies a lot of paper shuffling. The correspondence involved is collected in a so-called file wrapper, and studying a file wrapper can be quite revealing. File wrappers have always been open to public inspection, but in the past, getting hold of a file wrapper was expensive and cumbersome.

Nowadays, USPTO file wrappers can be consulted by going to the USPTO website (www.uspto.gov) and clicking on *Check Status* in the Patents column on the home page (check the status via the Patent Application Information Retrieval [PAIR] system). On the page that then appears, you click on *Public PAIR*, which brings you to the next page, where you have to type two words shown in funny letters. Once you have done that, you arrive at the page where you can enter a number and search. The number can be an application number, a control number, a patent number, a PCT number, or a publication number. After clicking SEARCH, you arrive at a multi-tab page. The tab "Image File Wrapper" provides what you are looking for. This could be the history of the patent, how it has repeatedly been continued in part, or why the claims in the granted patent are quite different from those in the Application Publication.

Similarly, European file wrappers can be consulted by going to an Esp@cenet website. By opting for Number Search and typing in the number, a page appears with the RESULT LIST. Clicking on the title displays a menu, including "View document in the European Register." Click this and a separate window called "Register plus" will appear; clicking there on "All documents" displays a list of documents from which a particular document can be selected to appear on screen.

Discussing edible oil processes in the chapters to come will provide me with further opportunities to highlight various patenting aspects while using the patents concerned as examples. That is less abstract than discussing them in this chapter. It has the disadvantage that the background information on the world of patents is scattered through the text, but a proper index can make up for that. I think that with the above, it should be possible to see any further aspects in their proper perspective; besides, I can imagine my readers may be getting a bit impatient and wanting to get on with edible oil processing, be it from a patent perspective.

1.4 Discussion

Manuscripts submitted to scholarly journals are more often than not peer-reviewed. To this end, the editor sends a copy of the manuscript to a specialist in the field and asks him for an opinion. Can it be published as such? Does it need amendment and if so, in what way? Or should it be rejected for publication? He may send the manuscript to two or more reviewers and only decide to publish the manuscript on the basis of unanimous recommendations, but even so, it regularly occurs that published articles have to be retracted or that Letters to the Editor highlight their mistakes. The article by Fleischmann et al. (1990) disclosing cold fusion may well be the article that most people remember in this context.

What about patents? They are examined before being granted. Does this examination prevent nonsense from being published? Sadly enough, this is not so and as with journals, nonsense occasionally slips through the net. At one stage, the Dutch Patent Office had special printed forms to tell an applicant/inventor that his invention would not be examined since it violated one or more laws of thermodynamics. Patent Offices that did not examine applications would therefore end up publishing a whole range of *perpetua mobilia.*

Examiners are bound by law. If the invention they have been asked to examine is novel, non-obvious, and useful, patent law tells them to issue a patent. It is not up to them to question the validity of the experimental evidence. This may happen at a later stage in court and if then an inventor is found to have cheated, he will lose his patent. In Europe, this approach can be taken during opposition, but in practice, it is very rare that experimental evidence is questioned or that evidence showing the opposite is presented. This is too technical for lawyers.

It is unlikely that a nonsensical invention will be confronted by any prior art disclosing identical nonsense. Accordingly, prior art is an unlikely ground for the rejection of a nonsensical application. A skilled patent agent should be able to present nonsense as something that is not obvious, thereby obviating another ground for rejection. Since violating the laws of thermodynamics can be made extremely useful, there is nothing to stop the patent from being issued. Even so, obtaining a nonsensical patent is a waste of money.

In Chap. 5, Sect. 5.2, I will discuss a nonsensical patent (Muralidhara et al. 2002) that claims that washing oils with water will remove free fatty acids. This is also claimed in Myong et al. (2007), a patent that even includes a mass balance showing that the gums contain the major portion of the free fatty acids in the crude oil that was washed with water. The explanation is simple. Washing crude oil with water removes phosphatides and some of them are acid. So the washing step lowers the acid value of the oil, which has been mistakenly interpreted as originating from a removal of free fatty acids.

The interesting thing about this is that there seems to be prior art for this nonsense. In that Erickson mentions (page 176 of Erickson 1995), "The FFA[49] of good-quality soybean oil will be in the range of 0.5 to 1.0%, which will be reduced by 20 to 40% in the degummed oil." He is not the only one. Charpentier wrote in 1991, "As I mentioned earlier, the main reason for degumming is to remove phosphatides,

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[49] In this monograph, I will use abbreviations without defining them in accordance with the guidelines issued by the *J. Am. Oil Chem. Soc.*

but it is important to notice the effect of degumming on the percentage of free fatty acids which obviously will result in a very important savings in neutralization.”

Apart from nonsensical patents, there are also totally useless patents. Take Chou and Chien (2007). They use fatty acid alkyl esters to extract triglyceride oil from raw materials such as rice bran. Consequently, they obtain a solution of oil in this ester and a marc[50] containing this ester. They isolate the oil by evaporating the ester from the solution, but they are completely silent about what they do with the marc. How do they recuperate the esters from there?

Why do people go for it? To have something in print and thereby create prior art that will prevent the competition from claiming something everybody would like? There must be cheaper ways of reaching that goal such as publishing an article in a scholarly journal. But then the aforementioned reviewers might reject the article, and besides, this reviewing business can take a long time. When applying for a patent, you immediately obtain a priority date, you know when your application is going to be published, and to create prior art, you only need a single publication that preferably will pop up whenever an Examiner carries out a literature search in that particular field.

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[50] I looked up “marc” in my dictionary and read that it meant “the refuse of grapes used in wine-making.” It is derived from the French *marcher*, to walk or tread, since that was how grapes were treated to give up their juice. In edible oil processing, the word “marc” is also used to indicate solvent–wet extraction residue.

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Chapter 2
Production of Oils and Fats from Single Cells and Animal Raw Materials

2.1 Introduction

A development that was hardly foreseen was the sudden emergence of biodiesel production and interest in renewable resources in general. The low yield per hectare of biodiesel made from vegetable oil has led to a search for other oils. Given the growing demand for fish oil in aquaculture feed preparation and its limited supply, it is therefore not surprising that single-cell oil (including algal oil) is receiving a fair amount of attention (Cohen and Ratledge 2010). It does not compete for agricultural land, in theory its yield per hectare could be quite high, and its fatty acid composition suits fish feed and can be made to suit biodiesel by partial hydrogenation. However, as pointed out in an editorial by Ratledge (2011), overcoming the many and often fundamental problems that make algal oil quite expensive will require massive attention.

This attention is reflected in the patent literature. Cultivating microorganisms on a large scale, harvesting them, and extracting their oil are all areas that are in their infancy, and their development leads to patent applications. Since a possible scale of operation of single-cell oil production is similar to that of current edible oils, I will discuss some of these patents. Most of these patents and their applications are quite recent. In fact, as illustrated by Table 2.1, the growth in the number of publications has been quite explosive, which means that this section will be out of date quite soon. This sudden and recent growth does not mean that microbial oil will be big business; it only indicates that there are a growing number of people who think that it will be and are betting on it.

When I waded through the lists of patents that are classified under C11B1 (Production of fats or fatty oils from raw materials), I came across several areas outside the scope of the present monograph. Accordingly, I will exclude all patents dealing with genetic modification of microorganisms or oilseeds to produce specific highly polyunsaturated fatty acids, and nucleic acid sequences encoding for something or other. These are primarily patents assigned to Monsanto, DuPont, Calgene, etc. I will also exclude patents concerned with the special fatty acids that can be

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4_2,

Table 2.1 Number of documents in my literature data base that relate to single-cell oil production

Year	No. of patents	Year	No. of patents
1991	1	2004	3
1995	1	2005	1
1997	1	2006	1
1999	1	2007	2
2000	1	2008	6
2001	3	2009	12
2002	2	2010	20
2003	1	2011 up to April	5

made that way, products containing these special fatty acids, patents that are concerned with minor constituents of triglyceride oils, their cosmetic or pharmaceutical applications, and products for which I only see a small-volume application, if any.

2.2 Microorganisms

Similarly, I will pass quickly over patent applications that deal with growing microorganisms. I have read several, and they can be quite interesting. According to Hartman et al. (2009), a logical place to locate an algal biomass plant would be next to a power station since the algae could use its waste heat and the carbon dioxide resulting from burning fossil fuel. To grow, they also need micronutrients that could be provided by sewage treatment effluent.

An inherent problem of the production of microbial oil is that after fermentation, the oil has to be isolated. It is a bit like extracting gold from seawater. The gold is there all right, but its concentration is negligible. Similarly, microbial suspensions resulting from fermentation reactions tend to be quite dilute and the oil content of the biomass may not be very high either. An early patent (Nakajima and Kondo 2001) describes a process that owes much to oilseed extraction processes. It starts with drying the microbial cells, then opens the cells by using an extruder, and extracts the extrudate with an organic solvent. The process is novel but hardly inventive. Nakajima and Kondo also applied for patent protection in Europe (EP 0 990 694 A1).

Bijl et al. (2004)[1] disclose a similar process. Looking at the INPADOC family of this patent reveals some 40 documents, among which is a European application EP 0 894 142 A1. This application has a priority date of 28 May 1996 and was published as PCT application WO 97/37022 on 9 October 1997. Comparing this

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[1] These inventors originally worked for the Dutch firm Gist-Brocades BV, a company producing yeast, penicillin, enzymes, and related products. It was taken over by DSM, another Dutch company which started as a state-owned coal mining company but evolved into a major chemical company moving into the life science area; hence this acquisition.

date with the priority date of Nakajima and Kondo (11 June 1997) shows that Bijl et al. (2004) have the earlier priority date. On the other hand, when Nakajima and Kondo filed their application, they could not have been aware of what Bijl et al. had invented, since their invention had not yet been published. This raises an interesting and very important question: Who obtains a right to what in countries where both apply for something rather similar?

Because the application by Bijl et al. had not been published when Nakajima and Kondo filed theirs, the disclosure by Bijl et al. does not affect the novelty of what Nakajima and Kondo disclose. They could not have known what Bijl et al. were up to. On the other hand, the European Patent Office could not allow the claims proposed by Nakajima and Kondo since Bijl et al. filed earlier. Accordingly, when examining the equivalent application (EP 0 990 694), the European Patent Office took the application by Bijl et al. into account and asked for the claims by Nakajima and Kondo to be modified by narrowing them in line with the specification so that they claim something different from what Bijl et al. would be allowed to do. The applicants obliged by specifying that the disruption of the cells and the granulation of the biomass be carried out at the same time. This reduces the scope of the patent and is therefore allowed.

So what was originally:

1. A method of extracting liposoluble compounds contained in microbial cells which contain liposoluble components, comprising drying microbial cells containing liposoluble components, **destructing and molding** the dried microbial cells by use of an extruder, and extracting the contained liposoluble component by use of an organic solvent

then became:

1. A method of … comprising drying microbial cells containing liposoluble components, **simultaneously disrupting and molding** the dried microbial cells … organic solvent ....

The same, narrower conclusion is also mentioned in the US equivalent (Nakajima and Kondo 2001), but in Taiwan, a country where DSM did not apply, the Nakajima patent (TW 533 235) was granted as applied for, that is, with the original, broader main claim. In countries where both companies obtained a patent, the Nakjima and Kondo patent depends on the DSM patent of Bijl et al. So if the Japanese wanted to use their patent in those countries, they could not do so without permission from DSM.

For a subsequent application (Bijl et al. 2006), DSM cooperated with Martek Biosciences in the US, but both companies continued to apply individually as well.[2] The joint application (Bijl et al. 2006) discloses the use of a desiccant such as silica that is to be mixed with wet biomass prior to solvent extraction. The solvent can be hexane but also a supercritical solvent like CO_2 or propane. All of these aspects indicate that the process disclosed by Bijl et al. is not a large-scale

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[2] Early in 2011, DSM acquired Martek Biosciences, so future applications will be by DSM only.

process. This is also hinted at by the products being claimed: triglycerides with a high arachidonic or docosahexaenoic acid content. Granulation of the biomass prior to drying to a dry matter content >80% has been claimed to significantly ease this drying (Bijl et al. 2009), and pasteurizing the biomass leads to improved oil quality (Schaap and Verkoeijen 2009). An earlier application by the same inventors (Schaap and Verkoeijen 2007) disclosing a deaeration process was rejected. On the other hand, an application from 2004 was granted (Bijl and Schaap 2008). It discloses the process of disrupting microbial cell walls and separating the microbial oil from the cell debris by centrifugation. The disrupting step comprises a high-pressure (150–900 bar) homogenization and may also comprise treating the cells with a cell wall–degrading enzyme.

An early industrial production of single-cell oil has been reported by Ratledge et al. (2010). It concerns the production of the Oil of Javanicus by the English company J. & E. Sturge in Selby, North Yorkshire. This oil, which contains 15–19% γ-linolenic acid, was made by fermenting *Mucor circinelloides,* and a low FFA content was assured by a kind of autopasteurization: Switching off the cooling system of the fermentor caused it to heat to 55–60°C, and holding it at this temperature for 30 min caused the lipolytic enzymes to denature. Then the biomass was dewatered by filtration and drying, and the dry biomass was extracted with *n*-hexane.

Since then, many approaches to produce single-cell oil have been published. Most of them comprise a method to isolate the cells from the broth in which they have been cultivated, a method to open/disrupt the cells, and a method to isolate the oil from the disrupted cells. However, some patents provide little detail about these methods by claiming, for instance, "… f) harvesting said *Crypthecodinium cohnii*, and g) recovering said single-cell oil" (Kyle et al. 1995). Another patent (Bijl et al. 2004) claims in step d) of the main claim that the oil is extracted or isolated from the dried biomass granules and then specifies in claim 4 that the oil is extracted using a suitable solvent.

It is not uncommon that early patents claim a whole range of different methods. After all, at the early stages of development, it is not yet evident in which direction future industrialization will evolve. So patent applications may just mention a method without going into detail to create prior art. Isolation methods comprise

- Spray drying of the broth (Gladue and Behrens 2002). If the broth is rather dilute, this method will be very costly.
- Using an inorganic flocculating agent such as an aluminum salt (Radaelli et al. 2009) or a constituent in the modified nutrient mix that triggers the flocculation of the algae in the plug flow reactor (Hazlebeck and Dunlop 2010a). The separator disclosed in the latter patent may include a belt press.
- Using an algae separator that removes the algae from the conduit (Hazlebeck and Dunlop 2010b). The detailed description does not mention what type of separator this might be. Consequently, it is impossible to repeat the process as claimed. If, therefore, somebody were to dispute the validity of this granted patent on the

grounds of insufficient disclosure, he might stand a good chance of having the patent revoked.

- Using a centrifuge to eliminate the excess water has been claimed in Echevarria Parres (2011). In fact, this application[3] describes the use of a second centrifugal separator to collect the oil from lysed cells. A more expensive process (Wu et al. 2009) harvests the cells by centrifuge and dries them by freeze-drying under vacuum.
- According to Lane et al. (2010), acoustic focusing can apparently also be used to concentrate algae before they are subjected to extraction.
- An indirect isolation method involves having the algae harvested by planktivorous organisms such as fishes, gathering these organisms, and extracting the lipids from these organisms (Morgenthaler 2010; Wu et al. 2010b, 2010c). Bivalves can also be used to harvest the algae (Stephen et al. 2010), and the oil that has been extracted from the organisms can also be converted into biofuel (Wu et al. 2010a).

The number of cell disruption methods disclosed in various patent and patent applications is even larger:

- The use of homogenizers has been disclosed in Hoeksema (2000) and Fichtali et al. (2007), whereas slotted rotors have been used by Echevarria Parres (2011) and Ott et al. (2010)
- Extruders, including twin-screw extruders, are mentioned in Nakajima and Kondo (2001), Bijl et al. (2004, 2009), and Streekstra and Brocken (2008)
- Some form of lysis is also quite popular (Ruecker et al. 2001; Gladue and Behrens 2002; Bijl and Schaap 2008; Nielsen and Wümpelmann 2008; Hazlebeck and Dunlop 2010b)
- Purely mechanical processes like grinding or laminating (Bertholet et al. 2002) are less popular, but
- Enzymatic processes are very much in favor (Bertholet et al. 2002; Kobzeff and Weaver 2003; Weaver et al. 2005; Bijl and Schaap 2008; Oyler 2010)
- Some applicants use high pressure (Weaver et al. 2005; Bijl and Schaap 2008) and/or ultrasound (Bijl and Schaap 2008; Echevarria Parres 2011)
- Steam rupture is advocated in Dunlop and Hazlebeck (2009) and a hydrothermal treatment has been disclosed in Bellussi et al. (2010)
- Heavy rollers are used in Hartman et al. (2009) and adiabatic compaction is disclosed in Thomas and Lindell (2009)
- Acid hydrolysis is used in d'Addario et al. (2010) and Hua et al. (2010), finally
- There is the electrical circuit to disrupt cells disclosed in Eckelberry et al. (2010) and the cryogenic milling disclosed in Fichtali and Sundararajan (2010)

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[3] The original application (WO 2010/090506) is in Spanish, which is rather obvious from its English translation.

The number of patents disclosing how to obtain the oil out of ruptured cells is also quite impressive:

- Oil can be obtained by pressing (Bertholet et al. 2004; Caspari et al. 2008; Fabritius 2009). Since the press cake will contain residual oil, the biomass can also be mixed with a cheaper oil before being pressed; this increases the yield of single-cell oil (Bertholet et al. 2002).
- Solvents can also be used, as in the early Oil of Javanicus production. So an early Martek patent (Kyle et al. 1995) also used hexane, and a later one (Kyle 1997) used hexane to extract the oil and a polar solvent, such as acetone, ethanol, or isopropanol, to clarify the crude oil. A subsequent Martek patent (Hoeksema 2000) discloses cell disruption by homogenization, followed by countercurrent extraction of the disrupted cell slurry in a packed column with a solvent that is immiscible with water such as hexane. In this respect, the process is quite similar to the one disclosed by Liddell (2001), the difference being that it does not use a packed column but high-shear mixing of the water-immiscible solvent in the slurry. Therefore, I would have expected the Liddell patent that was published as a PCT application on 6 February 1997 to be cited in the Martek patent (Hoeksema 2000) since the priority date of the latter is 15 December 1998, but this did not happen.

  In another Martek patent (Fichtali and Sundararajan 2010), the lipid is obtained from the extruded biomass by percolation extraction. This sounds all right, but when this percolation extraction is then further defined as selected from the group consisting of aqueous solvent extraction, organic solvent extraction, near-critical solvent extraction, supercritical solvent extraction, enzyme-assisted extraction, microwave extraction, and mechanical extraction, I start to wonder how to carry some of them out in a percolation mode.

  Various solvents are listed in Bijl et al. (2006, 2009). They are apolar and can be a C_3–C_6 alkane, preferably hexane, but liquid CO_2 and supercritical propane are also claimed; a subsequent DSM patent (Streekstra and Brocken 2008) also mentions hexane. A process aiming at a biofuel can use solvents that are not food-grade. Accordingly, Caspari et al. (2008) use water-immiscible solvents selected from the group of carbon tetrachloride, chloroform, cyclohexane, 1,2-dichloroethane, dichloromethane, diethyl ether, dimethyl formamide, ethyl acetate, heptane, hexane, methyl-*tert*-butyl ether, pentane, toluene, and 2,2,4-trimethylpentane[4] to extract the biomass.

  The press cake in Fabritius (2009) can also be extracted with an organic solvent, preferably hexane. The hydrolysis product disclosed in d'Addario et al. (2010) is also extracted with a non-polar organic solvent such as an aliphatic hydrocarbon.
- Several inventors use centrifugation to isolate lipids from the biomass as disclosed, for instance, in Bijl and Schaap (2008). Gravity separation is disclosed in Nielsen and Wümpelmann (2008), and further specified as centrifugal separation in a subsequent claim.

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[4] When copying this list, I noticed that the solvents had been listed alphabetically.

I found it interesting to note that quite a few patent applications in the field of single-cell oils obviously originate from people who are not very familiar with edible oil processing. They tend to focus on the microbiological aspects, neglect the oil processing aspects, and are insufficiently familiar with the typical oils and fats jargon. This jargon prescribes that we talk about diglycerides rather than biglycerides as in Mitropoulos (2008), who also purifies triglycerides by distillation. Another specification (Fisher et al. 2010) claims that platinum is a commonly used hydrogenation catalyst for edible oils; in Wu et al. (2010a), a prohibitively expensive process requiring equipment operating at up to 400 atm and 450°C is disclosed.

2.3 Fish Oil

As mentioned in the introduction to this chapter, fish oil is being used more and more as an aquaculture feed ingredient and source of nutritional supplements that are rich in long-chain, ω-3 fatty acids. This has led to the use of microorganisms for producing that kind of oil, but within the fish oil industry, it has also led to certain developments, notably the use of krill as raw material (Bimbo 2007). Krill is not a fish but belongs to the subphylum of the *Crustaceae* and the order of *Euphausiaceae*. Its estimated biomass is about 500 million tons. It is eaten by whales, seals, penguins, squids, and fish. Since krill feeds on phytoplankton, the fatty acid composition of krill oil makes it suitable as an aquaculture feed ingredient. Krill also contains astaxanthin, a compound that gives krill its reddish color and that can do the same to salmon when included in salmon feed.

The state of the art in the production of fish oil in the 1990s has been described by Bimbo[5] (1998). In fact, I leaned heavily on his description in Dijkstra (2007) when adapting his flowchart. The separation and purification of the fish oil have been described in more detail by Søbstad (1990). In the standard process, fish oil is produced by a wet rendering process by cooking the fish with steam and pressing the cooked fish to separate the liquid press liquor from the solid press cake. Adding an acid to the press liquor inactivates enzymes “that encourage unsavory taste and smell of said oil” (Crowther et al. 2001). Another way to produce “storage-stable marine animal oil free of undesirable odor or taste” comprises treating the fish with an antioxidant having peroxidase capacity and at a later stage washing the oil with a weak aqueous acidic solution (Rubin and Rubin 1991). The washing has to be “in a manner effective to cause methylamines to dissolve in the aqueous phase ....”

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[5] See also http://lipidlibrary.aocs.org/processing/marine/index.htm for the chapter on marine oils this author contributed to *The Lipid Library*.

Not surprisingly, (Rubin and Rubin 1991) is mentioned in the Search Report of another application (Aanesen and Breivik 2002), which discloses "a process for stabilising unsaturated oils (fish oil) which comprises treating a raw material (fish) with an organic acid prior to separating the oil from the raw material." However, there is a subtle difference in that Aanesen and Breivik treat the fish with the organic acid, whereas Rubin and Rubin treat the oil. Aanesen and Breivik also mention the use of an antioxidant, but they add it to the oil, whereas Rubin and Rubin add it to the fish. Accordingly, the patent (Aanesen and Breivik 2002) was granted.

The liquid is then purified by the removal of suspended solids in a decanter and then separated into fish oil and stickwater. The oil is washed, and protein present in the stickwater is recuperated by evaporation and mixing with the press cake that is then dried to provide fishmeal. A low-emission drier has been disclosed in Kunz and Vonplon (1991).

A normal cooking time is about 20 min, but in the Condec process, which uses a scraped surface heat exchanger (Søbstad 1990), this time is reduced to less than 2 min. The cooked material can be pressed but also sent to a decanter for liquid/solid separation. A piece of equipment that combines these two operations, cooking and liquid/solid separation, has been disclosed in an application by Piske (1996), whose employer only applied in Germany and did not pursue the application. Looking for this employer on the Internet to see whether or not the equipment was still on the market referred me to the Deutsches Museum in Bremerhaven.

Fish oil normally contains a fair amount of cholesterol. In the fish, this cholesterol is membrane-bound, and by allowing free oil to rise to the top of the strainer liquor and skimming it off, a fish oil is obtained that contains relatively little cholesterol (Oterhals 1996). A patent was granted in Norway, but it has not been maintained, and the applications in Denmark and Iceland never made it to granted patents. Another application (Süße 1997) that never led to a granted patent because of non-payment was only filed in Germany. My reason for mentioning it is that even though it did not make it, it still constitutes prior art and may be overlooked as such, having been published only in German. It concerns a relatively small piece of equipment that can be installed in a fish-filleting factory.

Fish guts are also deoiled in the process disclosed by Eriksson (2004). This application refers to a process (SE 8900206-7; publication number 463 315) in which fish guts are first frozen to below −18°C and then heated to above +30°C. This thermal treatment is reported to be highly effective for rupturing cells, and Eriksson improves this treatment by filling a basket with the frozen fish guts and placing the basket in a vessel that can be filled with water and heated. On top of the vessel, a conical cap allows oil to rise to its top so that it can be pushed out by the denser water. After the deoiling treatment, water is let out of the vessel, the cap is opened, and the basket is removed.

Yet another process for deoiling fish offal is the Friolex® process (Hruschka and Frische 1998). In this process (Best et al. 1999), fish offal is immediately immersed in aqueous alcohol (ethanol or isopropanol), with the result that enzymes are denatured and microbes are killed. Spoilage is therefore prevented and the resulting oil has hardly any fishy smell.

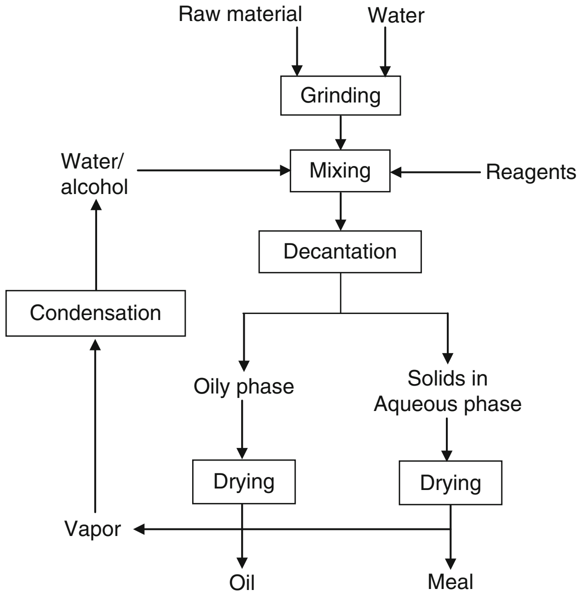

Fig. 2.1 Flow chart of the Friolex® process (Adapted from www.westfalia-separator.com website)

A flowchart of the Friolex® process is given in Fig. 2.1. This figure mentions "raw material" since according to the Westfalia publicity, the Friolex® process can also be used for oilseeds. However, I learned that the laboratory that developed the Friolex® process has been closed and that the industrial plant operating the process is used to extract oil from algae (K.-P. Eickhoff, personal communication).

Since phosphatides are soluble in aqueous alcohol, the resulting oil is likely to be degummed, but as far as I am aware, the literature does not report what happens to non-hydratable phosphatides. When an alkali is added as "reagent," the soap formed by this alkali will also dissolve in the aqueous alcohol; consequently, a neutral oil will be isolated in the decantation step. Moreover, the neutral oil losses that are inherent in the degumming process and in the alkali neutralization process are avoided since oil does not dissolve in the aqueous alcohol.

Sadly enough, no data are available on residual phosphorus levels.[6] The Westfalia publicity does not mention either how much water and alcohol should be added or how much energy is required in their evaporation.[7] In fact, the flowchart in Fig. 2.1 should also contain a purge for water since the raw material contains more water than the meal. Any alcohol present in this purge will be lost, so some fractionation may be needed to avoid this loss. So although the Friolex® process has interesting aspects, it also raises questions.

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[6] The patent (Best et al. 1999) reports that the oil in Example 11a had a 100 times lower phosphate (*sic*) content than the oil in Example 10, but no absolute figures are given.

[7] The patent data all refer to laboratory or semitechnical experiments.

Whereas the Friolex® process uses ethanol to obtain a sharp separation between the oil layer and the aqueous alcohol layer, another patent application (Strøm and Jøstensen 2000) disclosing the use of ethanol uses this ethanol to dissolve the oil. Since the solubility of oil in ethanol decreases sharply when the water content of the alcohol increases, the process requires a relatively large amount of ethanol, which would require extensive rectification in an industrial application. The patent also discloses an acid digestion of the fish with hydrochloric acid or acetic acid, both of which are corrosive and therefore necessitate the use of expensive construction material. It is therefore not surprising that the European application has been withdrawn. Only the Norwegian application resulted in a patent.[8]

The use of acids is also disclosed by Cloughley (2007), but whereas Strøm and Jøstensen (2000) operate at low pH (2–4) and use the acid to break down the biological material, Cloughley uses the acid (pH 3.3–4.0) to prevent microbial spoilage and lets the endogenous enzymes carry out a controlled autolytic proteolysis of the fish or fish waste. In addition, he wants to prevent lipolysis, so he adds green tea catechin flavanols as a lipase inhibitor; Cloughley only applied in the UK and later withdrew his application.

French patent 2 757 021, which is equivalent to (Barrier and Rousseau 2001), is not so much concerned with the production of fish oil but rather the production of deoiled fish meat for human consumption. Oil for human consumption in the form of a food additive or dietary supplement is the subject of Standal et al. (2004). It discloses a way to change the fatty acid composition of fish oil by controlling what the fish are fed; it needs 72 claims to describe all this.

The main claim of a patent granted to Saxby et al. (2004a) covers a

> method of removing oil from animal byproduct material, said method comprising the step of warming the temperature of said animal byproduct material to a temperature of less than 95 deg. C and higher than 55 deg. C, incubating and digesting said animal byproduct material in a first incubating and digesting step using the naturally occurring endogenous proteolytic enzymes of said animal byproduct to liquefy said animal byproduct material and centrifuging said liquefied animal material to remove said oil.

When I compare this main claim with the general description of the production of fish meal in a book that was published in the former German Democratic Republic (Papenfuß 1967), I read that in the standard process, the fish material is comminuted, then heated to a temperature of 90–100°C, and then sent to a press but that the Alfa Laval "Centrifish" process uses a centrifuge instead of a press.[9] So I cannot but conclude that the main claim in Saxby et al. (2004a) lacks novelty. In claim 3, the material is warmed to a temperature of less than 70°C, and this may be novel. Saxby et al. also applied for a product patent (Saxby et al. 2004b), but this application was abandoned.

I now want to use the main claim of Saxby et al. (2004a) to illustrate what could happen if the validity of this patent was challenged in a US court and what could happen to the European equivalent if it was opposed. In the US, the main claim might

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[8] The Espacenet INPADOC database does not provide information about the legal status of this patent.

[9] So I look up Alfa Laval and Centrifish in Google and where do I arrive? At Dijkstra (2007), where I quote Søbstad (1990).

well get revoked on the grounds that it is not novel, in view of the quotation from Papenfuß (1967) given above. Claim 2 in Saxby et al. (2004a) depends on the main claim and only specifies that "said animal byproduct is marine byproduct material." Since Papenfuß talks about fish material, this claim 2 is also anticipated and should therefore also be revoked. Claim 3 specifies that "said marine byproduct is warmed to a temperature less than 70°C" and is therefore novel in view of Papenfuß.

Now we should look at claim 4. It depends on claim 2, which depends on claim 1. It specifies that: "said first digesting step is subject to a pH between 6.5 and 7.5 and said time for said digestion is between thirty (30) minutes and forty (40) hours." Accordingly, the temperature of the method as claimed in claim 4 is between 55°C and 95°C (as specified in claim 1), the material is fishy (as specified in claim 2), the pH is between 6.5 and 7.5, and the duration has been specified with a very wide range. Does Papenfuß constitute prior art for this combination of process features? Not quite, but when we look at claim 5 in Saxby et al. (2004a), where the pH is controlled between 3.0 and 8.5, we can conclude that it certainly lacks inventiveness. Perhaps the judge might well revoke them on these grounds.

In Europe the situation could have been quite different. There claim 4 could have been formulated so as not to depend only on claim 2 but also on claims 1 and 3. So it could have read: "4. Method **according to any of the preceding claims** wherein said digesting of said marine byproduct material in said first digesting step is subject to a pH between 6.5 and 7.5 and said time for said digestion is between thirty (30) minutes and forty (40) hours." When judging this claim, the Opposition division has to look at all the combinations. It might go along with the US judge and conclude that claim 1 lacks novelty in view of Papenfuß but that claim 3, in which the temperature is limited to 70°C, is apparently novel. So in Europe, the combination of claim 4 and claim 3 might be allowed. In the US, this combination has not been spelled out and therefore does not exist and cannot be maintained. So the European system that allows claims to depend on more than one claim may cause more claims to survive opposition than the US system. This system requires that all the claims are spelled out over and over again to ensure all aspects are covered.[10]

There is also something wrong with claim 5 in the granted US patent (Saxby et al. 2004a). It reads: "5. Method as in claim 4 wherein said pH is controlled between 3.0 and 8.5." So claim 5 depends on claim 4 as quoted above. In claim 4, the pH range is specified as in between 6.5 and 7.5; or in other words, the range in the dependent claim is wider than in the earlier claim from which it depends. That does not make sense. A dependent claim should always be narrower than any claim on which it depends.[11]

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[10] I tend to read all these almost identical claims with a highlighter nearby to pick out the minor way in which each claim differs from the others.

[11] Since I had never come across a situation where a dependent claim specifies a wider range than has been specified in the claim on which it depends, I went to counsel (Dr. Scott Bloomer) and got as comment: "Good catch." The Examiner made a mistake by allowing claim 4 of the granted patent, which in the application read: "4. Method as in claim 2 wherein said digesting of said marine material is subject to predetermined pH and predetermined time conditions." Apparently the Examiner objected to this wording and insisted on a quantitative description with the unfortunate result that the next, dependent claim became too broad.

Now we finally come to the krill. Beaudoin and Martin (2004) work in a university and applied for a patent that extracts krill with acetone. This gives them an acetone extract that they evaporate to dryness to isolate the oil and an acetone–wet extraction residue that they then extract with a solvent selected from the group of alcohols and esters to obtain a second extract that is also evaporated to dryness to yield an oil with more phosphatides in it. From an industrial point of view, this process is useless since the solvent–wet extraction residue will have to be desolventized. How? With steam? That would lead to a condensate consisting of water, acetone, and the alcohol or ester that would then have to be separated into its various components by two (?) fractional distillations. Prohibitively expensive.

The applications by Krill A/S and Alfa Laval Copenhagen (Larsen et al. 2007; Ludvigsen and Breuning 2008) are far more likely to be used industrially, especially since they have been withdrawn and anybody who wants to can use them. They disclose a process in which krill is comminuted and then exposed to high-frequency waves to facilitate extraction. Thereafter, the multiphase system is separated into a solid fraction and a liquid fraction, and the latter is separated into an oil fraction and an aqueous fraction. Since Alfa Laval is one of the applicants, it is not surprising that the material is preferably heated in a Contherm® scraped surface heat exchanger, that a decanter is used to separate the solids from the liquids, that a centrifugal separator is used to separate the oil from the water, and that a clarifying centrifuge is used to recover the clean marine oil.

An application (Breivik 2008) discloses the isolation of phospholipids from krill. Its process consists of two steps, the first of which is a drying step for which it uses alcohol (methanol, ethanol, or isopropanol). This alcohol will dissolve some lipid that can then be isolated from the alcohol by evaporating the latter. However, the dried krill may still contain lipids so that it can be extracted again with supercritical carbon dioxide containing alcohol as entrainer. This latter method of extraction reveals that only small-scale applications with high added value are contemplated, such as (claim 17) “for use as a medicament and/or food supplement.” In another application (Breivik and Thorstad 2009), expensive techniques such as short path distillation, supercritical fluid extraction, chromatography, or an even more expensive combination thereof are used to isolate a krill oil with a high concentration of ω-3 fatty acids.

Although the method for making krill meal disclosed by Tilseth and Høstmark (2009) also mentions a pharmaceutical composition (claim 48) and a dietary supplement (claim 49), the application aims at large-scale processing, which is evident from the absence of solvents and a processing system comprising a ship (claim 45); the assignee is a Norwegian company.[12] In the process of Tilseth and Høstmark (2009), krill is mixed with water so that an aqueous phase is formed that comprises phospholipids and proteins. These can be isolated from the aqueous phase, and then

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[12] So the inventor whose name is written as Oistek Hostmark in the US and Australian Applicaton Publications, as +sten H|stmark in the Canadian application, and as Oeistek Hoestmark in the Espacenet family list has his name spelled as Øistek Høstmark in the PCT Application Publication. This last way of spelling looks the most likely.

the isolated fraction can be extracted to yield an oil with a high phospholipid content. A krill meal with a high astaxanthin content is also claimed.

The patent applied for by Denofa AS,[13] Norway, is remarkable in that the claims granted in the US (Jansson and Elvevoll 2010) are quite different from their European "equivalents." In the US, there are two claims, the first of which reads, "1. An improved process for production of oil from a biological material …," whereas the European main claim reads, "1. Process for separating and isolating nutritional elements from a material containing lipids and proteins …." The materials concerned can be almost anything: fish liver, whale blubber, soybeans, olives, microorganisms. The process prescribes a gentle treatment to minimize oxidation damage.

The green-lipped mussel *Perna canaliculus* can also provide lipids that are particularly rich in eicosatetraenoic acid (Chandler et al. 2009) by extracting (freeze-) dried flesh with a solvent selected from the group consisting of acetone, hexane, and ethyl acetate, concentrating the resulting miscella[14] by nanofiltration, and removing further solvent by rotary evaporation. The solvents used strike me as a weird selection in that acetone and ethyl acetate do not dissolve phosphatides, whereas hexane does. To get a mussel oil that contains at least 20% phospholipids, Häcker (2006) uses an azeotrope of alcohol and water in a first stage of his extraction process and follows this with an extraction by an anhydrous alcohol; he prefers the use of ethanol.

I do not know about this instance, but giving an established technique a new name is a good way to fool search machines and the Examiner relying on them. Maybe membrane filtration has been used for the above purpose, but calling it "nanofiltration" causes this potential prior art not to be revealed when just searching for "membrane AND filtration."

2.4 Carcass Fats

Rendering carcasses and meat trimmings is perhaps the oldest way to isolate a fat from an agricultural source. The main carcass fats are tallow from cattle and lard from hogs. Other carcass fats are mutton tallow from sheep and poultry fats from chickens, ducks (Dijkstra 2004), and geese. Carcass fats are produced by the rendering process in which the cells are ruptured by cooking and the resulting mixture is separated into various constituents. It can be considered a mature process,[15] and the amount of development going on in this area is modest. In fact, most innovations are concerned with processing equipment rather than the process itself. In addition, rendering plants are subject to veterinary inspection and have to comply

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[13] In some countries, the patent has been applied for by or granted to Marine Lipids AS, but this company has now been taken over by Denofa AS.

[14] The patent does not talk about a "miscella" but about a "solvent extract." It was written by somebody who was not familiar with the edible oils and fats jargon.

[15] The maturity of the field is also illustrated by the large number of references cited in recent patents. The Cargill patent (Schaefer et al. 1998) has about 60 references, several of which are more than 60 years old.

with many rules and regulations, which do not encourage technological development either. And finally, the loss of several traditional applications as a result of BSE (bovine spongiform encephalopathy) has reduced interest in tallow as a product (Woodgate and Van der Veen 2004).

Gilroy and Gilroy (1995) disclose a process in which the animal byproducts to be rendered are first of all cooked, after which crude tallow is extracted from the greaves in a high-pressure continuous press. Treating the crude tallow in a decanter yields a clean tallow stream and a sediment that is recycled to the press. According to the invention, some of the clean tallow is mixed with the animal byproduct (up to 10% of the feed) to improve the cooking efficiency.

What I did not understand about this process is why it uses clean tallow for the efficiency improvement rather than crude tallow. Using crude tallow would reduce the load on the decanter. The answer to this question is simple: prior art. So the specification argues, “It has been found that the quality of the meat and bone meal prepared from the greaves is relatively poor, and furthermore is not consistent. There is therefore a need for a method for cooking animal by-products in a continuous cooking process which overcomes this problem.” So the specification states that the prior art method was no good and that the invention is a highly desirable and urgently needed improvement.

I have great difficulty in believing this argument,[16] and I suspect that it has only been coined to be able to say somewhat later that we have surprisingly found that using clean tallow is the most perfect solution to this problem. Yes, it is more expensive, but it is worth it. In instances like this, the Examiner may also suspect the true reason why an argument has been forwarded, but there is nothing he can do about it. It is not even necessary that the examples provide experimental evidence supporting the argument.

When working on *The Lipid Handbook*, I visited a rendering plant in Eindhoven, the Netherlands. It was very much cleaner than the oilseed crushing plants I was used to. This visit also gave me an idea of the rendering process, its scale of operation, and what kind of equipment is used there. Although I felt quite at home and recognized several pieces of equipment and asked pertinent questions, this visit did not enable me to judge the advantages claimed in the patent literature. Even so, in my dealings with outside patent offices, I never came across a patent agent wanting to visit a plant to familiarize himself with the process he was describing or challenging. To me this indicates that patent agents often have even less idea about the scientific and technological background of their writings than I do.

A rendering process with some novel features has been disclosed by Vanhaecke and Decock (1999).[17] In this process, the comminuted material is heated above 100°C, causing the pressure to rise above atmospheric pressure. When the pressure is then

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[16] This is a polite way of saying that I don’t believe a word of it.

[17] According to the front page of this European Application, it has been applied for by a company called G. van Wijnsberghe en Co. in Veurne, Belgium. As the company is Belgian, it is more likely that the name should be written as “Van Wijnsberghe” with a capital V. That is the spelling I have adopted for the reference.

released, gases are released that may be quite smelly. According to the patent, these gases can be incinerated. The paste resulting from a solid/liquid separation step is dried and pressed to release oil, whereby drying the paste in a “fat bath drier”[18] is an option.

A kind of industrial deep fat fryer containing 4,500 gallons of oil that can be used for rendering is disclosed by Warren et al. (1998). The oil is heated to around 188°C and circulated through the cooker at a rate of 680–860 gallons (or about 3 m^3) per minute. This strikes me as an excessive rate of circulation. The poultry parts lose their fat, are removed mechanically from the cooker, and are pressed before being ground. This is an example of the dry rendering process.

Another example of a dry rendering process has been disclosed in (McDonnell and McDonnell 2003). This application discloses a dry rendering process specifying time and temperature treatments, but to me, the interesting point is that it discloses the use of a basket centrifuge to separate the greaves from the hot tallow. When working on the dry fractionation process, Pieter Maes and I discovered (Maes and Dijkstra 1985) that using a basket centrifuge led to a much drier filter cake than could be obtained on a Buchner-type filter such as the Tirtiaux vacuum belt. The basket centrifuge we used was a household juice extractor, and when developing a scaled-up process, we arrived at a conical sieve centrifuge fitted with a co-rotating scroll to control the retention time of the solid phase in the equipment. I have not come across this equipment being used in rendering plants but would not be surprised if its use led to drier greaves and increased oil yield. Comparing the performance of the sieve centrifuge with the membrane press in the separation step of the dry fractionation process showed that in some instances, the centrifuge produced a drier filter cake than the membrane press. Since presses used in rendering plants are not the high-pressure type, using a sieve centrifuge might improve matters provided small greave particles do not clog the filter screen. Such sieve centrifuges are also considerably cheaper than presses and have the further advantage that they operate continuously. They are also used in the potato starch industry (Maes and Dijkstra 1985).

The McDonnells (2003) are also concerned about sterilization in their dry rendering process and prescribe that the mixture of molten fat and greaves is held at a temperature of at least 120°C for a period of 10–20 min before the greaves are allowed to settle. Separation of the greaves from the fat is in several stages: first removing the liquid tallow from approximately halfway up the cooking vessel; then removing coarse material from the residue by passing it over a screen; and finally using a centrifugal separator (a basket centrifuge) for the suspension passing through the screen. Because of the preceding separation steps, the separator can be much smaller and therefore cheaper. Applications are limited to Ireland and the UK. They date from 2002 and 2003, and since I found no further publications, they have probably been abandoned. One of the McDonnells (McDonnell 2005)[19] purified

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[18] The inventors live in Belgium, a country that is not only famous for its chocolate confectionery but also for its chips (French fries).

[19] A patent (2 412 664 B) has been granted in the UK, but Inpadoc has no further information.

tallow by filtration using a drum filter, degassing the filtrate, and heating it to 137°C under a pressure of about 3 bar for a period of about 20 min. This should also rule out the risk of BSE infection.

A wet rendering process has been disclosed in (Margolis 1997). It describes a cooking vessel with a water inlet and a plurality[20] of suction tubes to remove the liquefied fat and other liquids from the meat after cooking. Looking at the patent family of (Margolis 1997) shows that it has 15 members. Some of them mention Joaquin Pelaez as co-inventor. Some have been applied for by Margolis, others by Taco Bell Corp, and there are also two kinds of titles. One possible reason is that the original US application was divided, but that does not explain everything. However, this case illustrates that looking at the patent family, which is fast and easy, may reveal aspects such as the importance the inventor or assignee attaches to the invention and/or how an inventor has managed to interest a company in his invention.

The wet rendering process invented by Margolis (1997) operated at atmospheric pressure. A wet rendering process operating at superatmospheric pressure has been disclosed by Schottelkotte (2002). In Europe, the application has been withdrawn, and in the US and Australia, it never got any further than the application stage either. The apparatus of this invention (claim 14) comprises many parts:

(a) a vessel with an entry end with an inlet opening and an exit end with a discharge opening
(b) an entry pump such as a piston pump (claim 15) delivering material into the vessel
(c) an exit valve such as a rotary valve (claim 17) that is "fluidly connected with the discharge opening" to let material out of the vessel
(d) an elongated conveyor inside the vessel[21]

This was the preamble and now we go on with the specifics:

(e) wherein the vessel can be pressurized and heated (is "connectable to a source of heat")
(f) "wherein the vessel is adapted to maintain minimal conditions within the vessel" or, in other words, wherein the temperature is maintained above 133°C and the pressure is maintained above 3 bar absolute (claim 20) and
(g) whereby material to be conditioned enters the vessel from the entry pump, passes substantially through the cylinder from the entry end to the discharge end, and exits the cylinder through the exit valve

This claim is, of course, unacceptable. The cylinder it refers to has not been mentioned before, and it appears like a bolt out of the blue. When drafting claims, always make sure that all items referred to have some kind of definition or context. It is therefore not surprising that the patent has not been pursued. In fact, the whole patent strikes me as an "armchair patent," but I may be wrong. The European Union

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[20] "A plurality of" is patent jargon for "several." Another way of saying the same is, "at least one" rather than "one or more." In the text this is then referred to as "the at least one suction tube."

[21] I find "inside the vessel" easier to understand than the original text, which says, "positioned within the vessel."

issues new regulations specifying a minimum temperature, and so forth, and so an invention is made from behind a desk (in an armchair) that prescribes a means of achieving this. Just combine a number of known aspects, make a few shrewd guesses, engage a clever agent, and there you are.

An inventive way to meet these EU regulations has been disclosed by Pinches (2008). He uses superheated steam having a temperature >220°C in a dry rendering process to sterilize the animal tissues remaining after removing the edible meat in a meat processing plant. The co-current process is continuous and because the steam is superheated, it evaporates most water present in the tissues. A first tallow stream is obtained from the reactor in which the tissue is moved forward on a rotating screen. Further tallow is obtained by passing the greaves over a screen and through a screw press.

Swift-Eckrich Inc. is a company in the precooked meat business. It produces frankfurters and wants to make them less fatty. So Singh and Trujillo (1996) comminute meat, heat it so that the fat is just molten, and feed it together with some water to a decanter. There a meat layer is formed against the decanter wall. Inside that meat layer, an intermediary boundary layer containing particles of fat tissue, meat, and water is formed; right inside, a layer of molten fat is formed. The amount of water used in the process suffices to separate the meat layer from the other layers, and the resulting meat has the same protein composition as the meat going in.

The use of a decanter in this process strikes me as quite ingenious. Its scroll will move gently through the meat layer and loosen fat particles just as olive oil in the paste is allowed to agglomerate during the malaxation[22] stage following the grinding step.

Singh and Trujillo (1996) heat the fat to more or less the body temperature of the animal when it was still alive. This has the danger that unwanted organisms are not killed. Therefore, Schaefer et al. (2000) include steps to kill these organisms by a "surface treatment with a heat transfer fluid provided at a temperature of between about 80 and about 150°C for between about 25 seconds and about 150 seconds."[23] This heat transfer fluid may be water (claim 11) at a temperature of 80–100°C (claim 12) or tallow (claim 13) at a temperature of 115–150°C (claim 14).

Another rendering process using a simple screen to separate the greaves from the fat has been disclosed by Eisner and Ernst (2005). It comprises an agglomeration stage in which the comminuted raw material is extruded to form strands with a diameter of some 4–8 mm; these strands are then combined to form a thicker strand that is chopped up in pieces that are easy to handle by the subsequent rendering and separating equipment. A binder can be included to prevent these pieces from disintegrating. The process produces a raw material for liquid fuel but is not limited to this application.

The Espacenet database has the advantage that it also contains Japanese patents and patent applications, but the disadvantage is that they are in Japanese. Fortunately,

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[22] None of the dictionaries I have at home mentions the word "malaxation," but in articles describing oil extraction from olives, it is the common descriptor of a slow mixing process that loosens oil from the solids present on the paste and breaks down the O/W emulsion.

[23] Be on the safe side. Soften every quantitative statement by including "about." Of course, claims 11–14 also included several "abouts," but for readability's sake, I left them out.

the “Bibliographic data” tab provides an abstract in English. These abstracts start with the PROBLEM TO BE SOLVED and then give the SOLUTION. Accordingly, Saito (2007) starts by claiming that conventional rendering processes cause the fat to degrade by hydrolysis and oxidation and then claims that heating the fat tissue with microwaves solves all problems. This struck me as a rather obvious solution, but since Espacenet does not provide any data on the legal status of Japanese patent applications, I had a quick look at google.com/patents and typed in “fish oil” and microwaves. This yielded a large number of hits, but glancing through them did not reveal anything in the way of prior art for Saito (2007). The process may still be considered as obvious though.

In a patent application filed by Mosley and Nickerson (2007), they describe a rendering process in which they grind the fatty animal byproduct material and then mix the ground material with an oil-absorbing clay product before drying this mixture. The dried material can be pressed to release some oil, but given the presence of said oil-absorbing material, this will be a reduced amount. Isn’t this defeating the purpose?

Whereas the above processes all aim at producing animal fat and a meat and bone meal, the process disclosed by Packer et al. (2009) is designed to produce cleaned ruminant stomachs to be sold as tripe. This cleaning also includes defatting, and a highly automated process for this aspect is the subject of this application.

Rendering leads to an aqueous effluent that may contain protein, fat, and other suspended solids. They can be precipitated by complexing them with an aluminate and then flocculating the aluminate complexes by adding a flocculating agent such as, but not limited to, pectin (Tarbet et al. 2002). The resulting precipitate can be removed and used directly as animal feed. It can also be rendered, yielding a tallow and a protein-rich material to be used as animal feed.

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Chapter 3
Production of Vegetable Oils from Fruits and Germs

3.1 Olive Oil

Olive oil has been produced for thousands of years by a rather simple process that starts by grinding the olives into a paste; a hammermill is the most common grinder. This paste can then be pressed hydraulically as such in between fiber disks separated by metal plates to yield a press cake called a "pomace" and a liquid phase called "must," which is a mixture of oil and vegetation water; or it can be diluted with process water and sent to a centrifugal separator (Di Giovacchino 1996, 1997). This can be a two-phase decanter feeding a centrifugal separator with a liquid stream to which some water has been added (Fuentes 1993), but three-phase decanters are also used.[1] A control system that can optimize both the two- and three-phase systems has been disclosed in Alba Mendoza et al. (2007). Because the phenols distribute themselves over the oil and the water phase, olive oil obtained by centrifuge has a lower polyphenol and *o*-diphenol content than oil obtained by pressing the paste (Di Giovacchino et al. 1994).

There is also a third type of extraction process called the percolation process that is based on the surface tension differences between oil and water (pages 35–37 in Di Giovacchino 1996). Extensive percolation leads to a pomace with about the same oil content as that attained after a single pressing. So the percolation can be combined with a second labor-intensive pressing, or preferably with sending the pomace to a decanter. Whereas common percolators use rotating steel plates, a novel type using rotating cylinders has been disclosed by Yildirim et al. (2009).[2]

Harvesting olives is a labor-intensive process. The oil content of the olive is only 22% (Boskou 1996), operating a small oil mill also requires a fair amount of labor,

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[1] See also http://lipidlibrary.aocs.org/processing/olive/index.htm.

[2] The inventor's name is printed as YILDIRIM, Nihat, and he lives in Gaziantep, Turkey. A patent to be discussed later (Yildrim 2008) gives as inventor YILDRIM, Nihat, who also lives in Gaziantep. I guess they are one and the same person but since I have no means to find out how his name is to be written, I use both names.

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and since the operation is performed in campaigns, equipment is often idle. All these factors cause olive oil to be the most expensive vegetable commodity oil. Even so, the annual world production has been between 2.5 and 3.0 million tons over the last 5 years.

Because of its high price, olive oil is strictly regulated; nine categories have been defined. The highest category is the "extra virgin" olive oil that must *inter alia* have an acidity ≤ 1.0%, a peroxide value ≤ 20, and a quotation ≥ 6.5 by a taste panel. If the oil does not meet the above acidity criterion or the taste is not "extra virgin" but just "virgin", it is relegated to the "virgin" category. According to Bianchi (1999),

> Virgin olive oil is obtained from the fruit of the olive tree solely by mechanical or other physical means under conditions, particularly thermal conditions that do not lead to alterations in the oil and which has not undergone any treatment other than washing, decantation, centrifugation and filtration to the exclusion of oils obtained using solvents or using adjuvants having a chemical or biochemical action, or by re-esterification process and any mixture with oils of other kinds. (Appendix to EC Regulation 1513/2001)

So the membrane filtration process mentioned in Mattei et al. (2004) stipulates the "physical treatment" in the patent title.

It is therefore not surprising that some patents claim a low-temperature treatment at below 35°C (Salvatore 1999), or between 20°C and 37°C (Van Buuren et al. 2004),[3] without heating the paste (Sallent Soler and Visa Sanfeliu 2003), or no temperature at all (Rapanelli 2006).[4] On the other hand, Garcia Martos et al. (2004) claim that heating the olives before they are crushed improves the oil extraction yield, but given the European Regulation cited above, it is doubtful if the oil thus obtained can still be called "virgin." That is certainly not the case for oil produced according to Jackisch (2005),[5] in which the enzyme pectinesterase is added to the paste obtained from olives that had not been destoned. Adding the enzyme amounts to a biochemical action, and that suffices for disqualification.

Another process prescribing the use of enzymes has been disclosed by Unilever (Lal Ganguli et al. 1998) to treat olive oil that is too bitter. The process entails that the oil is exposed to an emulsified water phase that exhibits enzymatic debittering activity; in my opinion, this amounts to using an adjuvant with biochemical activity. A second aspect of the patent application involves introducing polyphenols into the oil by emulsifying an aqueous solution of polyphenols in the oil and evaporating the water. The patent was granted but in 2010, it was allowed to lapse in those European countries where it had been converted into a national patent.

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[3] Jan van Buuren is a Dutchman. This means that he is listed alphabetically under the B as "Buuren J van." If referred to by his surname in a text, this is as "Van Buuren" with a capital V. Similarly, his co-inventor Karel Petrus Agnes Maria van Putte is referred to as "Van Putte" (capital V) and listed alphabetically as "Putte KPAM van" under P. To make matters even more confusing, Belgian citizens do not adhere to this system. So my former colleague, the late Willy Van Opstal, is always listed under the V and the Van is always written with a capital.

[4] This patent (Rapanelli 2006) has the "low temperature" in the title, but none of the 25 claims mentions a temperature.

[5] This patent application has been filed by Süd-Chemie AG, a company best known as a manufacturer of bleaching earth. Süd-Chemie is now part of Clariant AG.

In Spain, natural talcum powder (hydrated magnesium silicate) is allowed as a technological coadjuvant. Some enzymes can also be used in Spain, but then European legislation prohibits their use. Calcium carbonate is now claimed as a new technological coadjuvant (MoyaVilar et al. 2008) to facilitate the olive oil extraction process to yield virgin or even extra virgin olive oil, and a patent has been granted in Spain.

Olive oil contains some free fatty acids (FFA), and they are stronger than the carbonic acid in the calcium carbonate. Consequently, some of the FFA may well react with the carbonate and form calcium soap and carbon dioxide. The examples in the patent specification deal mainly with oil yield aspects[6] and report that the effect of the calcium carbonate on FFA is insignificant. I have my doubts. According to European legislation, the oil processed in accordance with MoyaVilar et al. (2008) should probably not be categorized as "virgin." However, that is no concern of the Patent Office, which is only concerned with the invention for which a patent is applied.

According to Patumi et al. (2003), removing the stones from the olive fruit before the grinding step increases the oil mill capacity and reduces energy requirement. The oil quality is the same, but the oil yield is reduced. Accordingly, machines have been invented that remove the stones from olives and cut up the olive pulp (Vitti 1994; Salvatore 1999). Subclaims in Düpjohann and Geissen (1993) are also concerned with stone removal. Cogat (2003) removes stones by quickly heating the whole olives to between 70°C and 95°C with live steam and cooling them rapidly by flash evaporation of water by reducing the pressure. The process also allows the fruit skins to be separated.

A more recent patent application concerned with stone removal is (Ouranos 2008). It was granted in Germany in 2007 as DE 10 2006 055 594 B3, but this patent will hardly provide any protection since its main claim is so detailed that it covers almost an entire page. Operating according to this patent but omitting a single mandatory aspect would effectively avoid infringement.

A pulp mill that can be used for olives with or without stones has been disclosed by Gurguc (2007).[7] It is a kind of extruder or expander fitted with both fixed and rotating crushing discs in the barrel segment where the olives have been compressed and "at least one crashing stone, which provides squeezing to the pulp of the crashed material, that is made of natural stone, preferably from granite, in cylindrical form, rotating together with the said driving shaft, providing aromatic taste addition by friction and squeezing of the material that come out of the space between the said crashing disc and fixed disc". In a subsequent claim, a second stone (a squeezing stone) is fitted around the crushing stone so that the material moves in between the two stones.

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[6] They even use Response Surface Methodology to arrive at quantitative correlations, but given my doubts about this method (Dijkstra 2010), I am likely to question any conclusions reached.

[7] This patent originates from Turkey. When I looked at the Turkish equivalent, I was surprised to see a different inventor/applicant: Ertekin Bilge. Don't ask me to explain.

Another type of crusher can be found in Yildrim (2008). It works on the principle of reducing volume rather than using friction, impact crushing, or the dead weight of a stone mill. Looking at Fig. 2 in Yildrim (2008) reminded me of the Wankel engine. According to the specification, the crusher can operate continuously. The use of ultrasonics to rupture the membranes in oil-bearing cells has been disclosed by Arnoud (1995), but the application was not pursued.

After crushing comes malaxation. One of the few patents I have come across that specifically deals with the malaxation step is (Van Putte 2002). Olive leaves are added to the malaxation mash in an amount of 5–50% by weight of the mash to fortify the resulting olive oil with at least 300 ppm of oleanolic acid.[8] Another patent application is (Van Boom et al. 2002), which strikes me as a typical recent Unilever patent in that there is no longer any chemistry involved, just mixing and stirring. Olives are mixed with one or more flavoring agents and crushed. The resulting mash is given a malaxation treatment and then separated, and "surprisingly we found" that the oil is somewhat flavored.

Yet another malaxation patent is (Picci 2008). It claims a malaxation process characterized in that the gas in the tank above the paste being treated contains between 6% and 12% oxygen so as to allow the activation of enzymes without giving rise to oxidation of the polyphenol and tocopherol products contained in the tank. A high phenolic antioxidant content of the olive oil is also claimed by Esteban Morales (2007) by adding a mixture of vitamin E and ascorbylpalmitate to the crushed olive paste prior to its centrifuging.

Another patent application concerned with oil quality is (Márques Gómez and Costa Escoda 2008). According to the inventors, oil is more stable in the olive paste than as pure oil. They therefore freeze the paste and only thaw it when they want to isolate the oil from the paste.

Quite a few patents disclose separation equipment. A patent applied for by Westfalia Separator (Düpjohann and Geissen 1993) is concerned with a process in which the olive paste is fed to a two-phase decanter, some water is mixed with the liquid leaving this decanter, whereupon the mixture is fed to a centrifugal separator. Something very similar has been claimed by Fuentes (1993).[9] It is therefore not surprising that the Westfalia patent was quoted as prior art, but since its application had not yet been published when Fuentes Martos filed his application, it was not considered as prior art. A patent was therefore granted, but in 1997, it lapsed. In another Westfalia patent (Hruschka et al. 2005), the fruit is first crushed and then subjected to pressure and a sudden release of this pressure before being fed to a

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[8] According to Wikipedia, this is a triterpenoid $C_{30}H_{48}O_3$: (4a*S*,6a*R*,6a*S*,6b*R*,8a*R*,10a*R*,14b*S*)-10-hydroxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,7,8,8a,10,11,12,13,14b-tetradecahydropicene-4a-carboxylic acid. I would like to include the structural formula in this footnote, but the word processing program I am using does not allow images to be inserted into footnotes.

[9] This is a very short patent having only a single claim. The detailed (!) description ends with, "On considère qu'il n'est pas nécessaire de s'étendre plus longuement sur cette description pour que n'importe quel expert en la matière comprenne la portée de l'invention et les avantages résultant de cette dernière."

decanter, whereby an extruder can be used to crush the fruit. Olives and avocado pears are mentioned specifically.

Westfalia Separator is not the only manufacturer of centrifuges. Alfa Laval in Sweden is also active in the field, and this led to an application (Klintenstedt 2004) that was also published as an Australian application that was allowed to lapse. In this application, Alfa Laval discloses a process for the production of olive oil. The preamble of its main claim, which covers two full pages, enumerates the steps of crushing the olives, malaxation of the paste, separation of the paste in a decanter, treating the oil thus obtained in a centrifugal separator to accumulate residual sludge at the radial outermost part of its separation chamber, and regularly desludging the separator. The characteristic part is concerned with this desludging step.

Yet another manufacturer of centrifugal separators is Pieralisi[10] in Italy. The abstract of Pieralisi (1996) reads as follows:

> A process and relevant centrifugal extraction equipment for the extraction of oils of different qualities from oily pulps, comprising the phase of separation of the different fluid and solid components making up the said pulp by centrifugal separation in a horizontal axis extractor, comprising the following phases: feeding of the product to the horizontal centrifugal extractor; centrifugation; retention in an axial direction of the lighter fluid component by radial means; drawing in an axial direction of the lighter fluid component retained axially and constituting a first quality of oil defined as first pressing; extraction in a radial direction of at least one further quantity of lighter fluid component consisting of oil defined as second pressing.

And indeed, claims 1–4 pertain to a process and claims 5–15 to a centrifugal extractor. I chose to quote this abstract to illustrate how incomprehensible English texts written by non-native speakers can be.

The specification refers to an earlier Italian patent (Pieralisi 1987) that discloses how paste is separated in a three-phase decanter and the solid phase is mixed with some vegetation water before being treated in a second three-phase decanter. This leads to two oil grades referred to as a first pressing and a second pressing. According to Pieralisi (1996), the oil quality of the first pressing is better than that of the second pressing, and it is therefore advantageous to keep them separate. The apparatus according to Pieralisi (1996) achieves this in a single piece of equipment that can best be described as a tubular centrifuge positioned coaxially inside a decanter. Oil obtained from the centrifuge is the first pressing oil, and the sludge leaving this centrifuge is mixed with water and then treated in the surrounding decanter, yielding a second sludge that is depleted in oil and the second pressing oil.

As only to be expected, the patent (Pieralisi 1996) has been cited in the application (Rapanelli 2001),which also discloses a decanter to be used in a two-stage separation process. In yet another patent of Italian origin (Pieralisi 2001), a centrifugal drier is used for treating the press cake. This can be a discontinuous basket centrifuge or a continuous conical sieve centrifuge. An extraction device that treats olive paste and has been designed in such a way as to facilitate cleaning has been disclosed by Rapanelli (2008).

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[10] This company is now called Macchine Agricole Industriali Pieralisi S.P.A., or Nuova M.A.I.P. for short.

Gall, who did not assign his inventions to a company, discloses a first invention in (Gall 1996). It concerns a centrifuge comprising a slightly conical tube that is fed with fruits at the narrow end, where they are also crushed. At the wider end, separate outlets are provided for the press cake and the liquid. A subsequent patent (Gall 1999) is specifically concerned with the adjustment of the separate outlets. Not surprisingly, the former patent (Gall 1996) was cited as reference in the later one.

Another private inventor is Sallent Soler (2003). His PCT application has has led to two granted patents in Spain (ES2217926 B1 and ES2238110 B1); when trying to read their claims, I was struck by the fact that these claims contain more than a single sentence. Apparently, there are countries that allow claims to be formulated in several sentences separated by full stops. As far as I understand the patent, it discloses a continuous process for the production of olive oil in which the olives are shredded and the resulting pulp is pressed against a cylindrical and "permeable extraction surface" (a kind of screen?). The movement of the liquid through this screen (?) is facilitated by applying a vacuum. The description occupies as many pages as the 35 claims.

Recently, Bonfiglioli (2007) disclosed a tractor-driven extraction plant to be used in between the olive trees. It comprises a crusher to produce a paste, a malaxation unit, a decanter that separates the paste into a cake and a liquid, and a centrifuge for the extraction of the oil from the liquid. Since the single tractor shaft drives all these rotating pieces of equipment, speed reducers and speed multipliers are included as well. Even more recently, an even smaller apparatus that is especially adapted to home users was disclosed (Padan et al. 2010).[11] It is basically a malaxation bowl that has been fitted with a filter.

Olive oil can also be clarified without using a decanter, centrifugal separator, or filter. According to Cerretani et al. (2009), filling an open tank with olive oil and bubbling an inert gas through it should suffice to clarify the oil. Theirs is a poorly written application. What is the point of specifying an inert gas flow rate when the amount of oil in the open tank or the tank volume has not been specified?

Finally, I want to mention a few patents dealing with avocado oil. One of them (Dolorantes Alvarez and Ortiz Moreno 2006) originates from Mexico. It discloses a process in which the avocado pulp is heated by microwaves to rupture the cells containing the oil before the pulp is pressed to separate the oil. The oil is also winterized. Its literature search report revealed prior art, and the application has not been pursued. The other patent (Msika and Legrand 2007) isolates the oil by drying the avocado fruit pulp and extracting the dried pulp. The oil can be subjected to a molecular distillation or to more standard purification treatments like chemical neutralization, bleaching, winterization, and deodorization. The oil then no longer contains acetogenins or furanic lipids. By mixing this avocado oil with a triglyceride oil that is rich in ω-3 fatty acids derived from linseed oil, fish oil, algal oil, or krill oil,

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[11] Quite unexpectedly, the "Background to the invention" in this application provides an excellent overview of olive processing and olive oil production.

a novel composition is arrived at that can be used as a dermatological or cosmetic agent or as a neutraceutical (Msika and Legrand 2009).

3.2 Palm Oil[12]

A US patent (Kooi 1991) discloses a continuous process for the production of palm oil. That it has been applied for in the US is remarkable since there are no oil palm plantations in that country. Furthermore, no equivalents valid in palm oil–producing countries like Malaysia or Indonesia are mentioned. The patent lapsed in 1995 due to non-payment of its maintenance fee. Even so, the patent provides an excellent description of the state of the art and especially its drawbacks. As a patent, it strikes me as not quite professional since it is too easy to circumvent.

Its main claim lists six consecutive steps; omitting or changing one of these steps is sufficient to avoid infringement. Instead of listing all steps, the inventor should have designated what he feels to be the essential step, for instance, the digestion of the palm fruitlets under pressure. This digestion should then have been the main claim. Subsequent claims could then have included other steps, and building up the patent that way would have made it much more difficult to circumvent.

This approach has been chosen by Graille et al. (1998), another patent granted in a country that does not have any oil palm plantations. Its main claim is limited to stating that the palm oil production process extracts the palm kernel oil at the same time; the second claim lists a series of six consecutive steps that are then further specified in subsequent claims. The last claim is a product claim that defines the mixture of palm oil and palm kernel oil by its fatty acid composition. For deep-frying purposes, this product is pretty useless since it will foam (Naudet et al. 1948), but interesterifying the product will eliminate this foaming tendency (Naudet and Desnuelle 1951).

The annual production of olive oil is some 2.5 to 3.0 million tons, which is only about 6% of the annual palm oil production of some 45 million tons. Nevertheless, I discussed more than 30 patents in the previous section, whereas the number of patents dealing with palm oil production is far less. Why is this? Could it be that there is less of a patent tradition in palm oil–producing countries than in countries producing olive oil? After all, a Malaysian patent can be obtained on the basis of a granted UK patent. If this is one of the reasons, things are changing since quite a few of the patent applications to be discussed below stem from Malaysia itself.

The first one to be discussed is Goh et al. (2004). It discloses a process to extract oil from the mesocarp fibers leaving the screw press. In general, these contain some 7–10% oil by weight on dry matter. However, they also contain too much moisture to permit solvent extraction. By drying them to a water content of 10%, they can be processed in conventional solvent extraction equipment such as

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[12] See http://lipidlibrary.aocs.org/processing/palmoil/index.htm for an up-to-date description of the production process of “palm oil”.

a rotary extractor. Other equipment for hexane recovery from miscella and hexane-wet fibers is also standard.

Another solution for the same problem is provided by Oku (2007).[13] It involves mixing the mesocarp fiber residue with a buffer salt solution ($5 < pH < 10$) and separating the mixture into three phases, the least dense of which is palm oil. This sounds easier than the extraction disclosed by Goh et al. (2004) since Oku avoids the use of hexane, the need to build an X-proof plant, and the need to dry the mesocarp fibers. There may also be disadvantages to the process disclosed by Oku, but since the application is in Japanese, I only have access to the abstract.

In a patent applied for by Flottweg (Ecker and Ertl 2007), a German manufacturer of decanters and the like, the use of a two-phase decanter for the clarification of the oil is advocated so that the sludge can then be dewatered separately and more effectively. If a three-phase decanter is used for this dewatering, the condensate from the sterilizer can be added to facilitate oil recovery. The process has been schematically represented in Fig. 3.1. A decanter that can be easily converted from a two-phase decanter into a three-phase decanter has been disclosed by a competitor in (Hruschka and Hulsmann 2009).

Another way to recover palm oil from this condensate and other aqueous streams containing small amounts of oil and fat has been disclosed in Woodley (2007). In this process, the wastewater stream is cooled to a temperature at which the oil/fat acquires a semisolid, non-colloidal state (partially crystallizes). The cool stream is then sent to a flotation vessel, where gas bubbles attach themselves to the fat particles, causing them to rise to the surface, where they are collected. The gas to be used is air that is dissolved under high pressure in a water stream that is then mixed with the water containing the fat particles. What I do not understand, though, is how cooling a stream of water containing some palm oil to a temperature of 45°C will cause these particles to be formed since the melting point of palm oil is more like 36°C.

Finally, there are three patent applications concerning the sterilizer to be used for fresh fruit bunches. One of these applications (Choong and Yeo 2006) discloses a vertical vessel that can be filled with fruit bunches from the top. After they have been introduced into the vessel, it can be filled with water to expel air; this water washes the fruit bunches at the same time. Another vertical sterilizer has been disclosed in (Lew 2008b). It comprises a movable arm to force sterilized material out from the sterilizer. The same inventor also disclosed a different sterilizer (Lew 2008a) that can be tilted to various inclined positions.

In his "Background to the invention," Kooi (1991) wrote that the prior art process for the extraction of palm oil uses the technology developed some 30 years ago in Africa. That means that at the time of this book's publication, the extraction technology is some 50 years old.[14] Some improvements have been made in those

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[13] The assignee of this patent is the Senior Creation College in Osaka. I wonder what that means.

[14] In fact, the process is much older because when Boekenoogen (1948) described the palm oil extraction process used in Sumatra before World War II, he listed the same elements of sterilization, threshing, mashing, and pressing. The crude oil was obtained by decantation and filtered before being shipped.

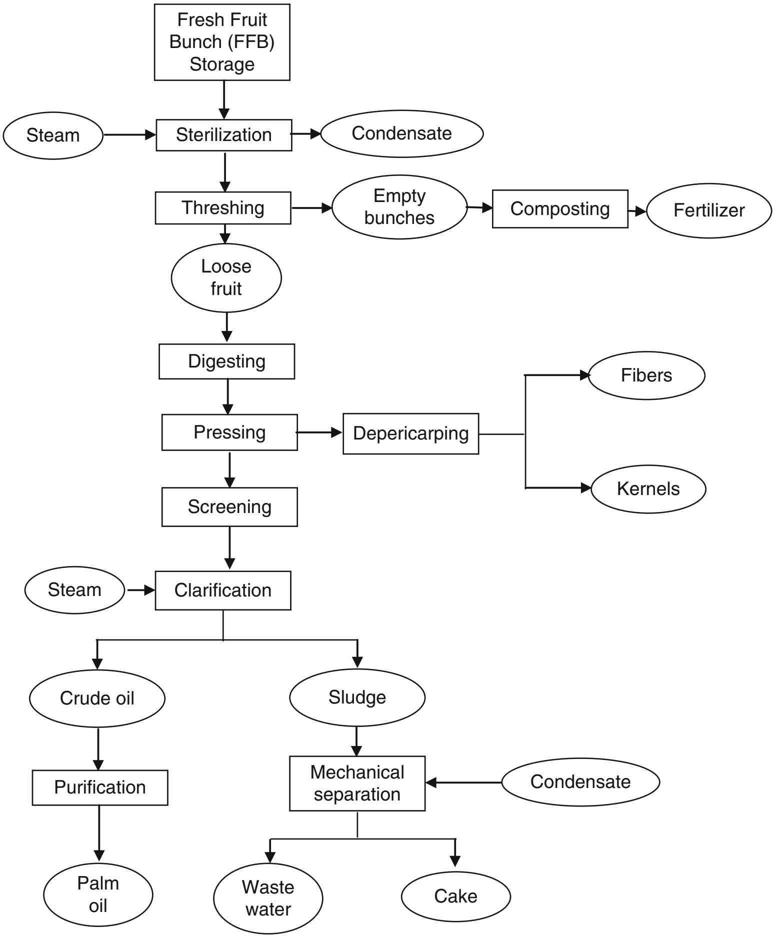

Fig. 3.1 Palm oil production flow sheet

50 years, but given the current level of production of palm oil, their number is surprisingly low. After all, a relatively small saving per ton multiplied by several million tons becomes a large saving in absolute terms.

Because the number of patents dealing with palm oil published per annum is increasing, I expect to see more developments in this field. Now it is common practice to sterilize the fruit bunches to prevent the oil from being enzymatically hydrolyzed. Is this the best method? According to Oo (1981), the lipolytic enzyme is not endogenous to the palm fruit but originates from wild yeasts. This raises the question of whether the treatment should target the yeast cells or the enzyme or both.

Once this question has been answered,[15] it will be clear how an improved pretreatment process can be de developed.

What holds for the sterilization step also holds for other poorly understood and therefore underdeveloped aspects of the whole palm oil extraction process. It is what I call “ripe for development,”[16] and in this context, I regularly quote[17] the French Nobel laureate François Jacob (page 10 in Jacob 1982):

> The capacity to judge what problems are ripe for analysis, to decide when it is useful to reinvestigate old territory, to reexamine questions that once were considered as solved or insoluble, remains one of the most important qualities of a scientist.

3.3 Germ Oils

In the wet corn milling process, the corn kernels are first steeped in water. This permits the germs to be removed as a pure fraction with a yield of about 7–8%. In general, they are processed in another plant, and so they are dried before being shipped there. The remainder of the corn kernel is then screened to separate the corn bran from the starch and gluten. The latter are milled and separated from each other by centrifuge. The wet milling processes are efficient in their use of corn since they produce numerous high-value corn products, such as corn oil, starch, corn gluten meal, corn gluten feed, and corn steep liquor. However, wet milling processes require very high capital investments in machinery.

The dry milling process does not start with a steeping step but immediately grinds the corn kernels and generates a ground product from which germs can be separated. As indicated by Table 3.1, the germs obtained in the dry milling process

Table 3.1 Composition of wet corn germ

	Wet milling process	Dry milling process
Yield (%)	7.5	12.0
Oil content %	38.7	23.0
Protein content (%)	13.6	15.4
Starch content (%)	7.4	19.8
Product yield*oil (%)	2.9	2.8

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[15] When my former employer Vandemoortele issued a new company brochure, some attention was also given to its R&D effort; it was on the last page. There I characterized the approach of my department as “application oriented but not afraid to take a fundamental approach.” To me, the distinction between fundamental research and applied research has always been artificial. The problem to be solved justifies the research, and the extent to which this study encompasses fundamental aspects is just a matter of efficiency.

[16] This is how estate agents around where I live describe a ruin of an eighteenth-century building in natural stone.

[17] In an address during the EuroFedLipid Congress in Strasbourg (2002), I used the quotation in connection with the bleaching process, and during the Congress in Graz (2009), I used it when suggesting that what happens to phosphatides during crushing was worth looking into.

constitute a larger proportion of the kernel than the germs obtained in the wet process; they therefore have a lower oil content. However, the products of germ yield and germ oil content are quite close for both milling processes. On the other hand, their absolute values are so low that it is self-evident that corn oil production should start with the dried germs. Extracting the kernel is limited to high-oil corn with an oil content of at least 8% (Ulrich et al. 2002). This process starts with flaking the kernel, the moisture content of which may have been adjusted to 10%.

Processing corn germs presents its own difficulties since the germs resulting from the wet milling process have an oil content of 40–52%. Flaking the germs to open their cells causes a substantial amount of fines to be formed, which hinders solvent extraction. Consequently, the process disclosed by Maza (2001) opens the germ cells by extruding wet germs having a moisture content of 15–20%. During this extrusion process, the water diffuses into the cells, cornstarch is partially gelatinized, and protein present is partially denatured. On the sudden pressure release at the extruder die, cellular water evaporates instantly, causing the cells to rupture and releasing the oil within the extruded meal. This can be extruded as pellets that are highly suitable for solvent extraction.

Van Thorre, a dentist by training and former Chief Science Officer of Biorefining Inc., concludes the background of his invention (Van Thorre 2006) by stating, “These types of processes have been developed without any regard for the elegant structures and architecture of the biomass. As a consequence, thousands of years of evolutionary development of the structures within the biomass have been ground, pounded, and pressed out of existence in order to extract oil or flour.” So we should not be surprised that, “The pericarp removal is performed in a manner that accommodates the symmetry of kernels of corn generally, and, for some embodiments, specific variations in symmetry of the kernels.” The application also contains a figure “that is subject to copyright protection. The copyright owner has no objection to the facsimile reproduction by anyone of the patent document or the patent disclosure, as it appears in the Patent and Trademark Office patent files or records, but otherwise reserves all copyright rights whatsoever.” I think it clearly shows the corn kernel structure, which is the reason why I have reproduced it as Fig. 3.2. The process disclosed in (Van Thorre 2006) carefully balances hydration and mechanical treatment of the corn kernel to attain the proper separation of its constituents.

Jakel et al. (2003) also treat corn in a special manner in that they do not flake the germs but optionally temper the corn, then crack the corn, and condition the cracked corn before finally extracting the corn. They claim that avoiding the flaking reduces the amount of fines. That may be so, but it may also “avoid” opening cells and allowing the oil to emerge.

A separation process using ethanol has been disclosed by Cheryan (2002), a specialist in membrane filtration. An ultrafiltration step of the corn ethanol extract yields a retentate from which the zein protein is recovered by evaporation of the alcohol. Its permeate can also be treated by membrane nanofiltration to yield an oil concentrate and an ethanol permeate to be recycled. Since the oil concentrate still contains ethanol, it still has to be evaporated, and so one could query whether the nanofiltration is a cheaper way of separating the ethanol from the oil than just evaporating all the ethanol.

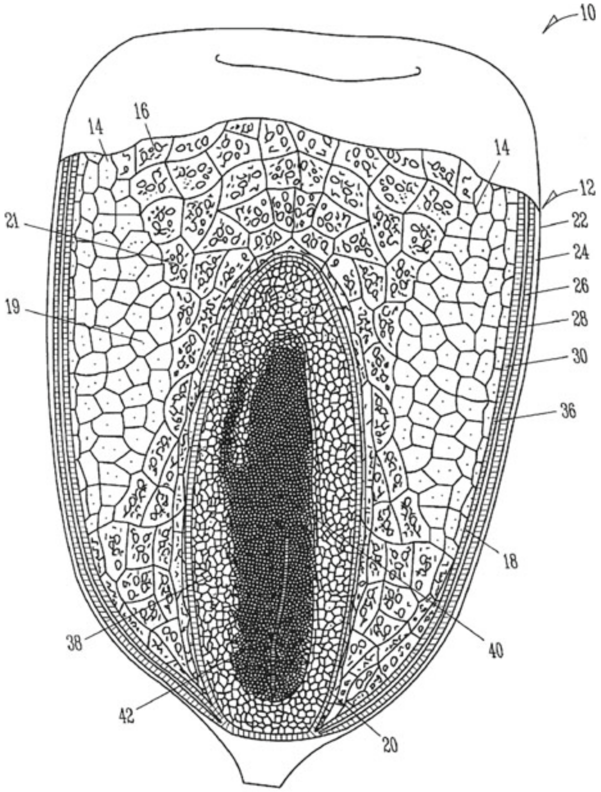

Fig. 3.2 10 Cross-section of corn kernel, 12 pericarp, 14 crystalline starch, 16 amorphous starch, 18 endosperm, 19 horny endosperm, 20 germ, 21 floury endosperm, 22 epidermis, 24 mesocarp, 26 cross cells, 28 tube cells, 30 testa or seed coat, 36 aleuron layer, 38 scutellum, 40 plumela or rudimentary shoot or leaves, 42 radicle or primary root (Fig. 1 from US 2006/0177551)

The main claim of the patent application (Binder et al. 2007) reads, “1. A de-oiled whole grain product.” Without carrying out a literature study, I suspect there will be prior art to this main claim. Literature articles reporting the composition of grains arrive at their oil content by taking grains, grinding them, and extracting the ground grain with a solvent. The extraction residue can be described as “a deoiled whole grain” and thus constitutes prior art for Binder et al. (2007). In fact, the above illustrates that prior art can be found in unexpected corners and that besides patent literature, there is other literature that also has to be taken into account. Which literature is relevant is obvious to an expert but less so for a patent agent – and for the Examiner as well. This is another instance where the patent agent has to rely on the expert knowledge, or rather common sense, of the inventor.

So the main claim may be untenable, but what about the others? Most of them are more concerned with corn, and some are quite fanciful. Claim 7, for instance, specifies that the germ should be deoiled by using a method selected from the group consisting of chemical extraction, expeller extraction, hydraulic press, mechanical press, carbon dioxide–assisted expeller extraction, and supercritical fluid extraction. It is unlikely that there is prior art for this claim, but how useful is it in practice?

High-oil corn is also the subject of (Van Houten et al. 2005), which is one in a series of patents and applications that also comprises (Van Houten et al. 2008) and (McWilliams et al. 2008) and that started with (Ulrich et al. 2002), to which the later specifications refer. They all fractionate the corn into a higher-oil fraction and a lower-oil fraction, but it is not clear to me why this description has to go on to explain, "wherein the lower oil fraction has an oil concentration less than that of the corn kernel and the higher oil fraction has a concentration greater than that of the corn kernel." I find them very difficult to read[18] and I have not really managed to discover what the surprise elements of the inventions are supposed to be.

Similarly, McWilliams et al. (2009) start with a high-lysine corn and process this into fractions by standard methods; surprisingly (?), some of these fractions have a high lysine content. I agree that such fractions are novel, but to me, they are hardly inventive. It is like somebody inventing a water-resistant paint that enables him to paint an object red, put it in the rain, and see that it stays red. That has several elements of an invention. If then somebody else changes the red pigment for a blue one, paints an object blue, puts it in the rain, and notices that it stays blue, that is predictable and not an invention although this particular blue paint is novel.

In the US, large amounts of corn are now used as a biofuel feedstock to be converted into ethanol by fermentation. This affects the availability of corn oil and also what material is extracted. Accordingly, one optimist applied for a patent (Winsness et al. 2007) starting with the following main claim: "A method of processing an oil bearing byproduct of ethanol production, comprising: recovering oil from the byproduct, and refining the recovered oil." Subsequent claims are more detailed, and on examination, they may well have to be incorporated into the current main claim, but it is doubtful if it will come to that.

US patent application (Randhava et al. 2008) discloses the use of an alkyl acetate as an extraction solvent. This can be the azeotrope consisting of 91.8% ethyl acetate and 8.2% water and having an atmospheric boiling point of 70.4°C. The application lists four methods of extraction that have been schematically represented in Fig. 3.3 (Fig. 2 in the application).

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[18] Paragraphs like "[0014] The whole high oil corn kernel comprises from at least about 3.5 wt%, at least about 4%, at least about 4.5%, at least about 5%, at least about 5.5%, at least about 6%, at least about 6.5%, at least about 7%, at least about 7.5%, at least about 8%, at least about 8.5%, at least about 9%, at least about 9.5%, at least about 10%, at least about 10.5%, at least about 11%, at least about 11.5%, at least about 12%, at least about 12.5%, at least about 13%, at least about 13.5%, at least about 14%, at least about 14.5%, at least about 15%, at least about 15.5%, at least about 16 %, at least about 16.5%, at least about 17%, at least about 17.5%, at least about 18%, at least about 18.5%, at least about 19%, at least about 19.5%, at least about 20%, at least about 20.5%, at least about 21%, at least about 21.5%, to about 22 wt% oil on a dry matter basis. In one embodiment, the corn kernel comprises at least about 3.5 wt% oil on a dry matter basis" are hardly inspiring. An even more unreadable example of verbosity of this kind can be found in Wang (2009).

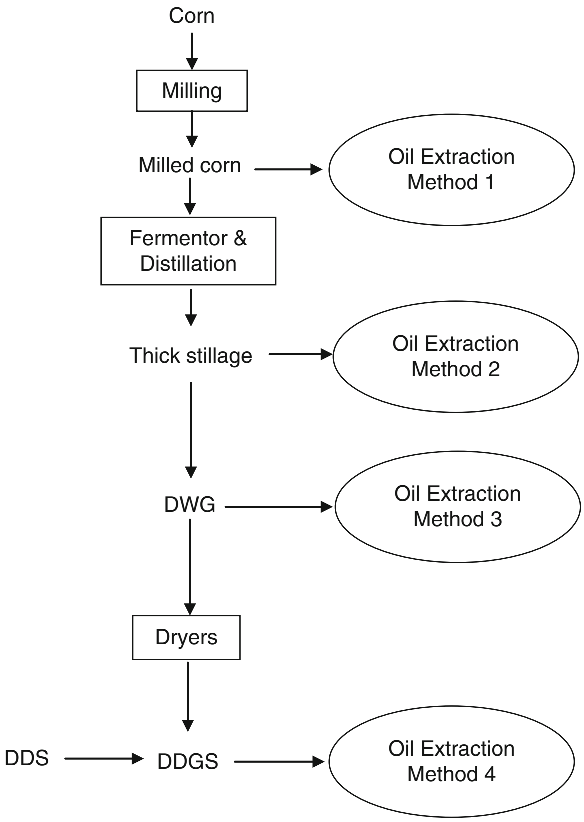

Fig. 3.3 Extraction methods according to Randhava et al. (2008)

The first method extracts the corn before fermentation. To this end, the corn is ground in a hammermill and extracted with the alkyl acetate solvent by mixing the ground corn with the solvent. The solvent containing water and oil is separated from the solids, and the oil is obtained by evaporation of the solvent. Solvent is also removed from the solids by stripping, which results in an oil-free and solvent-free substrate for fermentation.

The other extraction methods treat postfermentation material. This can be the so-called thick stillage (TS), the distillation residue of the ethanol distillation that contains about 10–20% of solids, both dissolved and suspended. Extraction is by mixing the solvent azeotrope with the TS and separating the phases in a settler. The solvent is recuperated as the azeotrope by evaporation of the light phase containing the oil and by treating the aqueous phase in a reboiler.

Oil extraction method 3 depicted in Fig. 3.3 treats the DWG (distillers wet grains). They are the solid fraction (about 35% solids) obtained when the TS is subjected to centrifugal separation, the liquid fraction being the so-called thin stillage. As in the previous method, a mixer/settler is used for the extraction, and the oil is separated from its solvent in a simple distillation column where the oil is the bottom product. The solids are fed to a reboiler unit, where the solvent is removed by stripping, condensed, and recycled.

The fourth method extracts the DDGS (distillers dried grains with solubles), the final byproduct of the ethanol production and drying process. It results when the solids remaining after fermentation are combined with the dehydrated bottoms of the alcohol still. The DDGS have a solids content of some 90%, just like the ground corn used in method 1 and oilseeds to be discussed in the next section. Removing the solvent from the extraction residue may therefore entail the same type of operation and equipment as used in oilseed extraction, but the application by Randhava et al. (2008) does not go into detail.

Such details are provided by Kemper and Subieta (2009), who disclose a process by which the DDGS are extracted with an organic solvent such as hexane or isohexane after they have been ground and pelletized. The equipment used to desolventize the deoiled, solvent–wet DDGS is a standard piece of equipment in which the solvent–wet pellets are fed to the top tray that is heated indirectly with steam. Live steam is also fed from underneath to remove the last traces of hexane.

Wheat germs are a byproduct of the flour-milling industry and arise mixed with wheat bran. Although the germ contains 30% oil, it only constitutes about 25% of the germ/bran mixture that consequently contains only some 7% oil, which is too little to produce wheat germ oil by pressing. According to De Sadeleer et al. (1998), the wheat germ/bran mixture is mixed with other oil-containing seeds or germs before pressing. This does not result in pure wheat germ oil, but at least a fair proportion of the wheat germ oil with its high α-tocopherol content is recovered from an otherwise useless byproduct.

Pure wheat germ oil, on the other hand, is obtained by a process disclosed in a recent application originating from Russia (Tikhonov 2010). The process starts with cleaning the germs, then dries them in a fluidized bed dryer for a period of 4 to 10 min, and then presses the germs in two stages at a pressure >120 bar and >200 bar, respectively. In an independent claim, another process is claimed comprising drying the germs to a residual moisture content of 5–9%; cold-pressing the germs and extracting the press cake twice with alcohol in a given germ-to-alcohol ratio; combining the extracts and evaporating them to dryness under vacuum at a temperature of 50–60°C.

My experience in dealing with the Russian Patent Office is limited to a single case, but the above application (Tikhonov 2010) reminds me very much of that particular case: To be accepted in Russia, claims had to be far more specific than I was used to. In a European application, I would have gone for a main claim mentioning just drying without specifying the final moisture content and mentioning just evaporating without specifying the evaporating temperature. I would have specified the residual moisture content and the evaporation temperature in subsequent, dependent claims.

If prior art also entailed a drying step, I might have had to distantiate myself from the prior art by specifying a range that is clearly outside the prior art, but otherwise, claims should be as broad as possible to make circumvention as difficult as possible. The main, independent claim should cover as wide a field as

Table 3.2 Rapeseed oil and rapeseed germ oil properties

Property	Rapeseed oil	Rapeseed germ oil
Chlorophyll (ppm)	12.4	2.9
Phosphorus (ppm)	525	190
Fatty acid composition[a] (%)		
C16:0	3.6	12.0
C18:0	1.5	2.9
C18:1	61.6	56.8
C18:2	21.7	21.4
C18:3	9.6	5.3
C20:1	1.4	0.4
C22:1	0.2	
Sterols (ppm)		
Brassicasterol	102	140
Campesterol	246	672
Beta-sitosterol	386	1,190
Isofucosterol	37	95

[a] The rapeseed oil values have been taken from Table 2.26 in *The Lipid Handbook*, 3rd edition, edited by F.D. Gunstone, J.L. Harwood and A.J. Dijkstra. Taylor & Francis Press, Boca Raton, FL

the prior art permits. Dependent claims narrow the field to the aspects that are most essential to the applicant, but the fact that Russia insists on including all kind of limitations into the main claim is just another illustration of the fact that patents are a national affair.

Oat germ oil can be produced by a process disclosed by Paton et al. (2000). The process uses about 15% pearlings produced when oat groats are abrasion-milled. When the pearlings are extracted with hexane, a dark oat oil is obtained, but when the pearlings are first extracted with aqueous ethanol, and the extraction residue is desolventized and then extracted with hexane, a light-colored oil is obtained. Other products like an enriched β-glucan can also be obtained from the oats.

The germ fraction in rapeseed is approximately 12%, and its oil content is about 37%. By crushing the rapeseed, a particle mixture is obtained from which a germ-rich fraction can be isolated. Oil can be obtained from this fraction in the standard manner, yielding more or less pure rapeseed germ oil (Nakatani et al. 2001). The composition of this oil is quite different from the seed oil (Table 3.2).

Soybeans can also be treated to yield a germ fraction, but since the germ constitutes less than 2% of the soybean, the fraction is very small. The germ or embryo fraction can be isolated according to a process disclosed by Kim et al. (1999) by cracking the soybeans and separating the cracked product into split beans and a mixture of hulls and embryos. This mixture is then sifted to remove a hull fraction and thereby obtain a second mixture of hulls and embryos that is enriched in embryos. Fractionating this second mixture by gravity force in a cyclone leads to a germ fraction with 90–97%

embryos. According to Beaver and Ites (2006), the isolation of this germ fraction is preferably incorporated into a production line that that produces soybean oil and low-fiber, solvent-laden white flakes. By subjecting the beans to a first crack and sifting the cracked product, a hull fraction that also contains the germs can be isolated. Aspirating this fraction produces the germ concentrate.

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Chapter 4
Production of Vegetable Oils from Oilseeds and Beans

4.1 Introduction

An obvious way to get an idea of the state of the art at a certain time is to browse through the proceedings of AOCS World Conferences held around that time. At such a conference focusing on emerging technologies, Penk (1986) presented a paper on the Lurgi Alcon® process and reported on the promising results achieved in Taiwan. In an attempt to find out whether any more plants were using this process, I consulted http://lurgi.com. This told me that Lurgi is now part of Air Liquide, and when I searched for Alcon,[1] there were no hits. Perhaps the Alcon effect is now more simply attained by using expanders (Lusas et al. 1990).

The next chapter in these proceedings (Pickard et al. 1986) deals with a Krupp process called VPEX.[2] Using the Google website and looking for VPEX and Krupp yielded a number of hits dating from around 1990 but nothing much later. Apparently, this highly promising process did not amount to anything either. So much for "emerging technologies." They illustrate that "Prediction is very difficult, especially about the future."[3]

Looking now at what was presented during the AOCS World Conference held in 1989 in Maastricht, the Netherlands, the presentation on mechanical pressing (Buhr 1990) gives a fair overview of current practices and advocates the use of expanders. They have indeed gained a solid position in oilseed processing. When discussing the basics of solvent extraction, Lajara (1990) stresses the importance of flake surface rather than the extent to which cells have been opened during the flaking operation. He mentions heat treatment of cracked seeds but is silent about the Alcon process (*vide supra*), and it was still too early for the Exergy® process

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[1] The A and L in the trade name ALCON® stand for AKZO and Lurgi, and not for Air Liquide.

[2] During an AOCS Annual Conference, I asked Harald Boeck of the Harburg-Freudenberger Maschinenbau if he remembered what VPEX stood for. He thought VorPressung/Extraktion.

[3] This is a quotation from Niels Bohr (1885–1962).

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4_4,

(Dahlén 1996a). He mentions that heat treatment causes more phosphatides to be extracted but neither dwells upon their hydratability nor raises the question of what could cause these phenomena. When talking about "Questions that no one is asking" (Dijkstra 2010), I listed this aspect as unresolved. The last paper in the Maastricht session was by Lusas[4] et al. (1990). In addition to discussing expanders, they reviewed a number of extraction solvents, including supercritical carbon dioxide and water, and mentioned enzyme-enhanced oil extraction and membrane processing of miscella. Twenty years later, the industry still only uses hexane, but isohexane has also been claimed (Turner and Venne 2003).

Does that mean that there were no changes at all in the last 20 years? Far from it, but several (most of them?) were not foreseen. In 1990, fish farming was still in its infancy, but today, the annual production of farmed fish has increased more than fourfold, to over 60 million tons in 2009. To ensure the nutritional equivalence of the farmed fish, their feed comprises fish oil. So whereas fish oil was formerly a byproduct of the fishmeal industry and used in Europe as a hardstock in non-vegetable margarines after having been hydrogenated, now the fish feed industry is the main customer for fish oil (Barlow 2004), which therefore commands its own price.

When discussing the production of vegetable oils from germs, I mentioned already that oils can be obtained by pressing and/or extraction with solvents and that the solvent–wet extraction residue can be desolventized. These process steps are quite common in the production of vegetable oils from beans and seeds. I will therefore discuss them in more detail in the present section.

I will also discuss some patents disclosing the use of solvents other than hexane, but I will exclude supercritical carbon dioxide or other solvents requiring high-pressure equipment. I have explained the reason for this exclusion in *The Lipid Handbook* (Dijkstra 2007) in Sect. 3.3.2.5: High-pressure equipment does not profit from an economy of scale and will therefore not be used industrially as long as solvents that can be used at close to atmospheric pressure are still allowed. Perhaps supercritical extraction could be used for very special, low-volume oils, but I will not discuss these either.

Scholarly journals like the *Journal of the American Oil Chemists' Society* or the *European Journal of Lipid Science and Technology* regularly contain articles about ways to make protein concentrates and isolates from oilseeds. When collecting the relevant patent literature, I encountered several patents dealing with these subjects. However, they fall outside the subject area of this monograph, and so I will not discuss them in detail.

Anhydrous milk fat, on the other hand, is an edible oil when molten and processed in large quantities. However, according to the European classification system, butter and butter products belong to class A23C15 and not to the class I have used when searching for the patents to review. This difference is also reflected in

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[4] A most valuable aspect of this article is its list of 122 literature references.

science and industry, which are very much segmented. You have dairy people dealing with butter and different people dealing with other oils and fats, but the latter are segmented too in that people dealing with olive oil also tend(ed) to have their own conferences, journals, suppliers, etc. Because butter and olive oil are expensive, their sectors are very much concerned with adulteration and its detection rather than with refining and modification, some aspects of which are even prohibited. Similarly, the European Union protects chocolate by allowing only a few fats that have not been chemically (!) modified to be mixed with cocoa butter. On the other hand, a certain rapprochement between the separate segments is unmistakable: Milk fat is being fractionated, olive oil is nowadays included in some margarine fat blends, and blends of milk fat and vegetable oils are also used to make spreads. Accordingly, I will discuss some milk fat aspects when discussing fractionation.

When discussing the production of fruit oils and germ oils in the previous chapter, I used the individual fruits as section headings, but doing so for seed oils would lead to undue repetition.[5] I therefore decided to discuss the production of vegetable oils from beans and oilseeds by discussing processing steps rather than by discussing the individual oilseeds, with the exception of cocoa beans. In fact, I will lump together several processing steps like drying, conditioning, crushing, dehulling, and flaking – and call this section “Oilseed pretreatment” – for the simple reason that the literature does as well. In a subsequent section, I will discuss processes using equipment such as extruders, expanders, and expellers. Then I will devote sections to the use of enzymes, extraction solvents, the solvent extraction process, and desolventizing in the broadest sense. Literature that does not fit into any of these sections will be discussed under “Miscellaneous.”

4.2 Oilseed Pretreatment[6]

Whereas olives have to be processed in campaigns, oilseeds have the advantage that they can be stored so that they can be processed year round. Accordingly, capital invested in oilseed processing is used more intensively, and this also means that it can often be justified more easily – or, rather, with less difficulty – than in the case of olives. When seeds are to be stored, their moisture content must not exceed a maximum limit, to prevent the growth of fungi and the concomitant lipase formation resulting in FFA increase. Accordingly, trade specifications have been agreed that also permit the raw material to be graded and disputes to be settled. Since drying further than required by these specifications constitutes an expense for the supplier, raw material reaching the oil mill hardly varies in moisture content.

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[5] In my opinion, the latest edition of Bailey’s *Industrial Oil & Fat Products*, F. Shahidi (ed.), suffers from this drawback, which is one of the reasons I did not purchase this handbook; price is another.

[6] See also http://lipidlibrary.aocs.org/processing/seedprep/index.htm.

For soybeans, this is 14% by weight (Woerfel 1995). A more general rule states that it should be 17% on an oil-free basis.

Soybeans have to be dried after having been cleaned. A dryer comprising a moving, porous conveyor belt has been disclosed in Stevenson and Anderson (1992). Hot air is blown through nozzles positioned beneath the belt run. This air causes the granular material (soybeans) to form a spout, and a stationary stave extending into the material downstream of such a spout generates a void that allows mixing to occur with less air pressure at the jet.

Another type of dryer has been disclosed by Hilt and Thomas (2001); it was developed for drying fertilizers, but it is also suitable for oilseeds. It contains an assembly of parallel vertical plates that are double-walled to accommodate the heat exchange fluid that indirectly heats the beans and evaporates the water. A gentle stream of dehumidified gas is fed in between the plates, picks up moisture, and leaves the dryer close to saturation. Consequently, this type of dryer requires less energy than commonly used by hot-air dryers since the amount of hot air leaving the dryer is far less. In a similar type of dryer (Jordison and Rozendaal 2007), the double-walled plates have holes through which the gas can move in a direction that is perpendicular to the plates. This means that the gas moving through beans that are still fairly cold is hardly heated; this constitutes a further energy saving; the perforated double-walled plates will probably be more expensive.

Drying can be combined with heating and cause the hulls surrounding the oilseed to dry and shrink away from the meat part of the seed. Then the heating and drying treatment tends to be called "conditioning." However, conditioning is a rather loose term since it is also used for the process in which the oilseeds that may have undergone a pretreatment are prepared for the flaking step. During this step, the seed material needs to be fairly soft and pliable to reduce the power consumption of the flakers. In (Givens et al. 1989), a conditioning process is disclosed in which raw seed material is allowed to fall down a rising preheated gas stream. This stream slows the rate at which the oilseeds fall and thus increases their residence time in the conditioner. Staves extend across the conditioner so that the oilseeds will ricochet off the various staves and bounce randomly from side to side; this will cause the hulls to be detached.

How to separate the loose hulls from the oilseed meat has been disclosed in (Moses 1994). He uses an apparatus with a central core that is again fitted with staves[7] to further loosen any hulls that are still adhering to the meats. Presumably this is an improvement on an earlier patent (Moses 1991) that set out to do almost the same. The apparatus disclosed by Anderson et al. (1998) combines the functions of the previous two pieces of equipment. It conditions the oilseeds, loosens hulls, and also separates the loosened hulls from the oilseed meats.

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[7] Yes, Givens et al. and Moses assigned their invention to the same company (Crown Iron Works), and both patents have been drafted by the same patent office (Nawrocki, Rooney & Sivertson). Hence the same jargon and the use of the word "stave," for instance. This also holds for three further patents (Moses 1991; Anderson et al. 1998; Anderson 2002b) to be discussed next.

Another development in the field of oilseed pretreatment has been disclosed by Anderson (2002b); this is a “reissued patent.” As far as I am aware, reissuing patents is something typically American. The description of the reissued patent starts with the statement, “Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates an addition made by reissue.”

According to the USPTO Manual of Patent Examining Procedure,[8] Section 1402:

> A reissue application is filed to correct an error in the patent which was made without any deceptive intention, where, as a result of the error, the patent is deemed wholly or partly inoperative or invalid. An error in the patent arises out of an error in conduct which was made in the preparation and/or prosecution of the application which became the patent.

In subsequent paragraphs, it becomes clear that changes can only be made to the claims. This is clearly illustrated by Anderson (2002b), where the original claim 1 has been deleted and replaced by new claims 2–6.

The patent itself refers to the Bühler-Miag dryer[9] and claims that it provides an improved structure that is usable in combination with said dryer to increase the efficiency thereof. The invention refers to a modular system, uses heated gas as the drying medium, and has a pump to forward this gas through the apparatus.

A more recent Bühler patent (Heeb and Keller 2006) refers to the so-called hot dehulling process. In this process, the meat shrinks away from the hulls after having been dried rather than the hulls shrinking away from the meat. After having been hot-dehulled, they are ready to be comminuted.

A comminution apparatus has been disclosed by Rothmann (2005). It comprises

> at least two crushing rollers that are driven in opposite directions between which is formed at least one engagement pairing of a radial cross-piece of one roller and radial groove of the other roller, whose flanks are arranged parallel and at an angle between 0 and 90° to the longitudinal axes of the rollers such that a parallel gap is formed between two neighbouring flanks, characterised in that the flanks are provided with a threaded profile.[10]

The equipment is marketed as the Multicracker®, which I highlighted as a recent development in 2009.

A dehulling apparatus for sunflower seeds has been disclosed by Rasehorn et al. (1992), an application made by the former East German company Schwermaschinenbau-Kombinat “Ernst Thälmann” (hence the abbreviation SKET).[11] It discloses a multistage dehulling process whereby the hulls are separated from the meats by sieving and electroseparation, and insufficiently pure fractions are reprocessed.

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[8] This manual can be consulted at the USPTO website, but understanding it fully requires specialist knowledge.

[9] The text probably refers to Fetzer (1987) but does not say so in so many words.

[10] This is part of the main claim and the abstract.

[11] This company was well known for its sunflower seed dehulling equipment. This company now forms part of the CPM Group that also owns Crown Iron Works, which company recently took over the solvent extraction technology from Harburg Freudenberger Maschinenbau GmbH.

Another sunflower seed dehulling apparatus has been disclosed by von Rotenhan (2003). It comprises a drum in which a shaft with spikes rotates and thereby causes the pressure in the drum to build up. It also comprises means to limit this pressure buildup to avoid oil leaking from the meat at this stage of the milling process.

In a quite early patent, Strop and Perry (1990) disclose a totally different seed treatment process that also comprises a drying step. I find this a most intriguing patent since it subjects the oil to an acid degumming treatment before it is forced to leave the oilseed. Normally, the crude oil resulting from oil milling is degummed with water and then treated with an acid to decompose the non-hydratable phosphatides (NHP) to arrive at an oil that can be physically refined after bleaching. Now, the crude oil resulting from the oil milling process according to the invention has such a low phosphorus content that it can be physically refined as such. It need not even be bleached. In the Strop & Perry process, oilseeds that may be dehulled or not or germs are mixed with oil and comminuted by grinding. A degumming acid is added, water is added, and the mixture is heated under vacuum, causing some water to evaporate. The resulting slurry is then separated in a centrifuge to recover the "cooking oil" with some of the oil that was present in the raw material and a solids fractions that can then be processed in a screw press or immediately extracted; the oil resulting from the extraction is recycled to the centrifuge. According to the flow sheets in (Strop and Perry 1990), the oil leaving the centrifugal separator only requires washing and filtering before being steam refined, cooled, and stored. This means that fully refined oil is produced without the separate steps of degumming, neutralization, and bleaching.[12] This indicates potential savings, but it also means that the process raises a fair number of questions.[13]

- The inventors "extract" the solids fraction by pressing. When a laboratory press is used, this still leaves about 10% of oil in the press cake. Is it possible to extract the cake emerging from a screw press with a solvent to increase oil yield?
- If so, what is the quality of the oil obtained by this solvent extraction? Can that oil be physically refined without prior degumming and/or bleaching?
- How critical is the amount of "cooking oil"? What is its function? Heat transfer?
- Is the process applicable to other raw materials than the soybeans and corn germs reported in the patent?
- How much water has to be added and evaporated? For energy reasons, this should be as little as possible.

Studying the process in more detail will reveal more questions. The patent was allowed to lapse in 1994, and an earlier patent (US 4,808,426, which was also granted in Europe as EP 0 267 933) was sold to The Dupps Company and expired due to non-payment of its maintenance fee in 2001. The inventors have not published

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[12] That is assuming that the results as reported can be repeated.

[13] I saw in the AOCS 2009 Directory that the first inventor was a member, so I sent him an e-mail to tell him that I was interested in his process, but I did not receive a reply. In the 2010 Directory, his name was no longer mentioned.

anything about their process in the *Journal of the American Oil Chemists' Society* since a search only revealed the latter patent as a reference.[14]

One of them is mentioned as first inventor of a rendering process (Perry et al. 1981), in which a partially deoiled solids residue is cooked and dewatered. In two further patents (Strop 1991, 1993) originating from the same original application, water and an acid are added to the oilseed slurry. This acid hydrolyzes glucosinolates, leading to "a substantially toxic-free feed." Instead of an acid treatment, a sodium hydroxide treatment of seeds has also been disclosed to detoxify tobacco seeds (Li 2010).

Another question raised by Strop and Perry (1990) is to what extent the low-NHP content of the resulting oil is caused by the addition of a degumming acid or by the temperature profile during seed conditioning. At that time, it was already known that treating soybean flakes with live steam (Kock 1981) in the Alcon® process leads to a crude oil with an increased phosphatide content but with a much reduced NHP content, so that after water degumming, less than 10 ppm of phosphorus is left (Penk 1981). Expanders have a similar effect (Lusas and Watkins 1988; Zhang et al. 1994). Even drying soybeans in a fluidized bed causes more phosphatides containing less NHP to be extracted (Tosi et al. 1999).

Carolina Soy Products, Inc. also heats soybeans to produce an oil that has a low NHP content, but protecting its know-how was a lengthy and thus expensive process. In Fig. 4.1, I have indicated the family tree of the documents that resulted from a single application. This application was filed in February 2001 and it claimed both a process and the resulting product. So the Examiner felt that it had to be divided.[15]

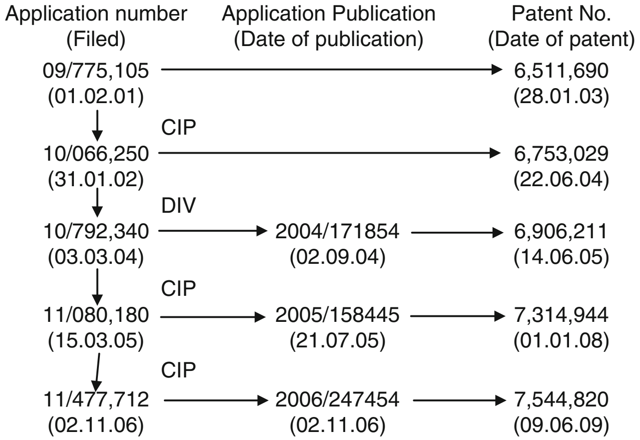

Fig. 4.1 Family tree of application publications and patents resulting from a single application by Carolina Soy Products Inc. (CIP is continuation in part; DIV stands for divisional application)

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[14] The fact that there was a hit proves that the search worked. Since it did not reveal any articles by the inventors, it indicates that there are none.

[15] This information originates from the file wrapper I could access from my desk.

Accordingly, the first two patents (‘690 and ‘029[16] or Tysinger et al. 2003 and Tysinger et al. 2004, respectively) claim a process, whereas the next two (‘211 and ‘940 or Tysinger et al. 2005b and Tysinger et al. 2005a) claim a soybean oil. The last one (Tysinger et al. 2009) has a different title, “Vegetable oil process,” and covers oilseeds in general. It is still tied to the original application filed in 2001.

Accordingly, the patent that resulted from the original publication and that was published in early 2003 was not regarded as prior art for the last application, which was filed at the end of 2006. In addition, the fact that the subject matter in the last application was wider than in the original application to which the new one was tied did not prevent the new one from being granted. This is only possible in the US (Bloomer 2004) and is very different from the European approach, where any publication before a filing date is regarded as prior art and where a granted patent can never have a wider scope than the application from which it originated. It is therefore not surprising that many people used to the US system of continuation in part tend to encounter unexpected problems in Europe.

However, by amending its Rule 36 as of late 2010, the EPO[17] also offers the possibility of filing a divisional application if the Examiner concludes there is lack of unity of invention and provided the division is filed within 2 years after the Examining Division’s first communication. That way, the EPO has moved slightly toward the US position, but large differences remain.

The US is also unique in that it provides inventors with a year’s grace. In the US, an inventor may disclose his invention in an article or a written publication and provided he files his patent application within a year, these prior disclosures are not regarded as prior art. Not so in Europe. Anything published before the filing date is regarded as prior art even if the inventor published it himself. Consequently, whenever an application for a patent outside the US is contemplated, it is advisable to ask potentially interested customers to sign a confidentiality agreement before discussing the invention with them.

As in previous patents, Tysinger et al. also heat their oilseeds to 160–190°C, and the resulting oil has to be heated under vacuum to a temperature of 230–260°C, but the older of the two patents (Tysinger et al. 2003) specifies that the oil has to be extracted in less than 30 s when the beans are heated, whereas the later patent (Tysinger et al. 2009) does not specify a maximum extraction period but specifies that the oil be expelled mechanically instead. This oil is defined as a solvent extraction-free and caustic refining-free oil, but even so, a dependent claim specifies, “the process of claim 1, wherein said oil is mixed with a weakly basic solution to remove calcium and magnesium.” In the text, this weakly basic solution is defined as an aqueous solution of an alkali metal hydroxide, and that is exactly what I call “caustic.” Moreover, as shown by Hvolby (1971), calcium and magnesium are only

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[16] I use a shorthand notation here that is also used by the USPTO in its Office Actions.

[17] http://www.epo.org/law-practice/legal-texts/official-journal/ac-decisions/archive/20101029.html.

removed completely at pH 14; when a weak base is used, their removal is likely to be only partial.

The patents also claim a *trans* content of less than 1%.[18] When describing the physical refining process, the specification states, “Deodorization, which is essentially a form of physical distilling,[19] in which the oil is subjected to high temperatures under a vacuum for a short period of time, which is sufficient to remove the flavor-causing components, but insufficient to break down non-hydratable phospholipids.” There is no mention of the use of a stripping medium, and including this in the claim would not have reduced its scope since without it, a low residual FFA content of the oil could not have been reached anyway.

Pellets can be produced by using an extruder to heat rice bran to 100–200°C under a pressure of at least 500 psi (35 bar) for a short period (5–20 s) in the absence of moisture. The oil in these pellets is stable because the lipase has been inactivated; on solvent extraction, they yield more oil than the non-extruded bran (Lee 1991).

For rapeseed and sunflower seed, the change in phosphatide composition has been linked to the denaturing of phospholipases (Veldsink et al. 1999), but that does not explain the increased phosphatide content of the crude oil. Beyer and Heilmann (2003) are far more outspoken in this respect:

> “By means of the deactivation, the increase of NHP in the crude oil during the recovery in the oil press and also in solvent extraction is wholly or largely prevented. As a result, the phosphatide content in the crude oil recovered can be reduced by means of a simple water treatment for degumming such that the oil degummed can directly be supplied to the physical refining.”

In their process (Beyer and Heilmann 2003), flakes are charged into a transporting mixer, where they are treated with steam and/or water. They leave the mixer after a period of 5–50 s having a temperature of 90–110°C and a moisture content of 8–20%. Then the flakes are annealed, dried, and cooled before their oil is recovered. The inventors assigned their invention to Metallgesellschaft AG, the former parent company of Lurgi. A certain similarity between their process and the Alcon® process is obvious.

Snyder et al. (1992) dry soybeans at temperatures below 130°C, and preferably around 70°C, to a moisture content of about 9–10%. Then the dried beans are dehulled and ground into a fine flour, which causes the moisture to be further reduced to 6% or less. Rapid extraction of the flour with hexane prevents the phosphatides from being extracted; they remain with the flour. Lecithin[20] can then be isolated by extracting the hexane–wet flour with aqueous ethanol.

The patent by Snyder et al. (1992) originates from a university and is based on laboratory work. It is not clear why the soybean oil contains only 30–50 ppm

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[18] This reminds me of the peanuts served during a cross-Atlantic flight. They were also *trans*-free. Quite some years ago, I was served “cholesterol-free” peanuts on a similar occasion.

[19] I thought that all distillations were physical.

[20] This must be phosphatidylcholine (trivial name lecithin), since this phosphatide is ethanol-soluble. Phosphatidylinositol does not dissolve in ethanol.

phosphorus. Early work on extraction (Karnofsky 1949) showed that the phosphatide content of oil increased when the solvent extraction was continued, but again, no mechanism was suggested and it is not certain that repeating those old experiments would lead to the same observations and conclusions.

Several of the effects described above are not limited to soybeans. In 1996, Dahlén presented a poster disclosing the Super Expro® rapeseed pretreatment process (Dahlén 1998). The pretreatment involves heating the rapeseed flakes to well over 150°C for approximately 20 s. It is interesting to note that the process was originally developed to produce protected (bypass) rapeseed meal by giving rapeseed meal a short heat treatment. So a heat-treatment unit was inserted between the desolventizer/toaster and meal cooler/dryer. Then it was found that the same protein quality improvement could be obtained by giving this heat treatment to the full-fat flakes and that, in addition, the NHP content of the oil decreased markedly; this is what has been patented (Dahlén 2000). The heat-treatment unit is a GEA-Exergy Steam Processor (Münter 2007), which originates from Chalmers University, Gothenburg, Sweden, and it is used to dry a wide variety of mainly agricultural products. Subjecting non-flaked seeds to a dry heat treatment (Elstner 1988) followed by expelling and extraction also leads to a low-phosphorus oil that also exhibits a low FFA and low peroxide value. Enzyme inactivation is felt to have caused these improvements.

Rapeseed dehulling has been studied by Thakor et al. (1995), who concluded that moistening the seed with steam and drying the moistened seed in a fluidized bed resulted in maximum dehulling efficiency. They more or less confirm earlier publications by Schneider describing the mechanism of extracting oil from rapeseed (Schneider and Rütte 1989, 1990). They also made an invention (Schneider 2001). After removing metal and stone, they separated the rapeseed in three fractions: a fraction containing straw and foreign seeds; a pure rapeseed fraction; and a fraction comprising broken seeds. They discarded the first and the last and dry the pure rapeseed fraction to 4.5–5.5% moisture while making sure that the temperature did not increase above 40°C. Then the dried seed was crushed by a roller mill and fractionated by sieving; the meat fraction was moistened, flaked, and cold-pressed.

Dielectric heating (both high-frequency field and microwave field) has also been used for pretreating oilseeds (Oberndorfer et al. 2000), but its effect on the oilseeds and oil quality has only been discussed in qualitative terms. Quantitative data on the effect of microwave heating on the phospholipids have been reported by Yoshida et al. (1997). However, a 2:1 vol/vol chloroform/methanol mixture was used to extract the lipid fraction from the beans instead of hexane, and some of the samples seriously degraded during the microwave heating.

A process to recuperate some heat has been disclosed by Homann (2009). Accordingly, the hot press cake leaving the screw press is cooled by air before being extracted at a much lower temperature, and the air leaving the press cake cooler is used to heat the seeds. The application is being examined, whereby a lecture by Schumacher (1988) will be taken into account as possible prior art.

4.3 Extruders, Expanders, and Expellers[21]

I have the impression that the above three terms lack a clear definition and are therefore used rather indiscriminately. The apparatuses they refer to have in common that they comprise at least one screw that moves the material being treated through a barrel. Inside the barrel, the material can be compressed or heated; a solvent, steam, or another gas can be added to the material; oil may be squeezed out through a cage in the barrel; and at the end, the material or residual material leaves the barrel by being forced through a die.

My first encounter with an extruder was when I worked as a material scientist for ICI. It was fed with thermoplastic granules that were melted inside the equipment and forced as a melt through a die at the other end to form pipes or profiles. Manufacturing plastic film also started with extruding the plastic. Heat to raise the temperature of the granules and to melt them was supplied by an electrically heated mantle and by friction inside the extruder.

An expander is quite similar to an extruder except that it causes the material to increase in volume when it leaves the die. At Vandemoortele, we used an expander when manufacturing snacks from flour like corn flour that popped at the exit die. Expellers are extruder-like, but they allow liquid to leave the barrel through slits when the material being expelled is under high pressure; they are also referred to as a "screw press."

Manufacturing extruders and the like is a highly specialized activity and that also holds for describing their salient features in patents. I remember that the patent department of ICI Plastics Division employed a patent agent who was specialized in the configuration of extruder screws used to process polythene, a subject that kept him fully occupied. Presumably, the Patent Office employed a similar specialist. I am not such a specialist, and therefore I now list the patents and patent applications I have identified that deal with screw configurations without any further comment:

- A combined expeller/expander is disclosed by Williams (1990).
- After having pointed out that the above apparatus does not work on oilseeds that have a low-fiber content, Kemper (1997)[22] discloses an improved apparatus that also aims at collecting oil from oilseeds with a high-oil content and producing uniform pellets of reduced oil content.
- A screw press in which the screw tip can be exchanged without removal of the extractor head has been disclosed by Linsgeseder (1997).
- An expeller producing a press cake in the form of easily extractable pellets is disclosed in (Skuras 1997).

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[21] See also http://lipidlibrary.aocs.org/processing/expanding/index.htm.

[22] In most patents, dependent claims indicate their dependence by stating, for instance, "Apparatus according to claim 1, wherein…." This patent application uses a different way of expressing the same: "Apparatus **as recited** in claim 1, wherein …."

- Yet another screw press has been disclosed by Strähle (1998).[23]
- A screw press into which extraction solvents can be introduced has been disclosed by Foidl (1999).
- A dual screw expeller has been disclosed by Rigal et al. (1999).[24]
- Yet another dual screw expeller has been disclosed by Bouvier and Guyomard (2000).[25]
- A screw press has been disclosed by Fries (2006), whose application has also been published as a German *Gebrauchsmusterschrift*.[26] This concept can be translated into English as a "utility model." In Germany, a utility model has a 10-year term of protection, and the novelty requirements are less stringent than for a full patent.
- Carbon dioxide injected in the screw press is disclosed by Homann et al. (2006), but its amount is limited.
- A screw press with specially oriented slits has been disclosed by Juwet (2007).[27]
- In a Russian patent (Koshevoj et al. 2007), carbon dioxide is fed in a subcritical state into oil-bearing material being expelled.
- A German application publication (Schedlbauer 2007) discloses a screw press wherein the oil leaves the press through sintered metal.
- An apparatus for injecting a fluid into a screw press has been disclosed by Floan and Smallridge (2008).
- Yet another screw press with fluid injection such as supercritical carbon dioxide has been disclosed by Schulz (2008).
- A Brazilian extruder of vegetal (*sic*) oil that "works in a different way from existing squeezers" has been disclosed by Galvao (2009).

In oilseed processing, the individual cells in the seed have to be ruptured to enable the oil to leave the material either as such during pressing or in solution as miscella during extraction. To this end, the seeds or germs are flaked, but that can leave some cells intact. This can lead to incomplete oil extraction and/or a slow release of hexane from the toasted meal. Accordingly, processing soybean flakes in an extruder or expander has the advantage that it ruptures any cells in the flakes that are still closed and the additional advantage that it increases the bulk density and the porosity of the material to be extracted (Pavlik and Kemper 1990; Kemper 1995); the latter two factors increase the extraction plant's capacity.

The role of expellers is also concerned with the opening of cells and with decreasing the extraction plant's size by diminishing the amount of oil left in the press cake. How far to extract oil by screw pressing and thus how much oil to leave for extraction depend on the economics involved. At a certain stage, expelling more oil

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[23] This patent has only been published in German.

[24] This European publication is in French. and the only other family member is a French patent.

[25] This patent was published as WO 97/43113 and has also been granted in Germany as DE 697 01 151 T2. Accordingly, in addition to a French text, a German text is also available.

[26] Figure 2 in the application is a very beautiful exploded view of the equipment.

[27] This patent has only been applied for in Belgium and the text is in Dutch.

requires much more power and also reduces the capacity of the screw presses. Then it becomes more economical to extract that oil with a solvent since operating a slightly larger extraction plant does not cost that much more. The picture is more complex with some crushers producing cold-pressed oil to satisfy a consumer demand that I regard as entirely artificial. This shifts the position of the economic optimum. To control the oil temperature, a water-cooled sleeve can be fitted around the screw press barrel (Kemper et al. 1994). Another way of cooling has been disclosed by Floan and Smallridge (2008) in which a fluid is injected into the barrel. This fluid can be a coolant (claim 7), it can comprise a solvent (claim 9), it can be injected at near-supercritical conditions (claim 10), and it can comprise carbon dioxide (claim 11). The press oil can also be filtered and cooled under cooled conditions (Alén et al. 2002).

Cold-pressed grapeseed oil has been disclosed by Fleming (2004), who later abandoned his application. He starts with drying marc while avoiding high temperatures. In this respect, he differs from what vintners around me do. They recuperate the alcohol present in the marc by distillation to produce an eau de vie, but sadly enough, they char the distillation residue. This causes the oil extracted from this residue to be dark and difficult to bleach. Fleming avoids this darkening, which his process has in common with (Eckert et al. 2007), a US patent that also discloses a process for producing cold-pressed grapeseed oil.

This patent has a German priority and was published as a PCT Application (WO01/10987) that listed 17 claims, including product claims. When we compare these with the granted US main claim[28] (Eckert et al. 2007), we note that the latter is a combination of original claims 1 and 3–11; consequently, it can be circumvented in many different ways and is therefore completely worthless.

That also holds for the PCT application (Tys 2009) originating from Poland. Like Russia (*cf.* my remarks in Chap. 3 on Tikhonov 2010), Poland apparently also has a tradition of writing very detailed main claims. The application (Tys 2009) starts by specifying the rapeseed cultivar, when the seeds should have been harvested, the moisture and chlorophyll content of the seeds, the maximum level of seeds with brown coloring, etc. The claim is so detailed that I asked myself to what extent all these requirements are really mandatory since if they are not, the scope of protection is so narrow as to be useless.

Schulz and Suhr (2006) disclose a process to expel oil from preconditioned oil-bearing material that involves at least three screw-pressing steps. In between these steps, the partially deoiled material can be reconditioned. They claim that increasing the number of screw-pressing steps reduces the residual oil in the press cake but does not increase the electrical energy requirement of the process; it does increase the investment though.[29]

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[28] There is a typing error in this main claim as well. It specifies –80°C rather than just 80°C. Time for a reissue?

[29] Not surprisingly, the patent has been applied for by a manufacturer of screw presses.

Another process has been disclosed in a PCT application (Burger et al. 2005) that has been abandoned. It aims at extracting plant oil from plant material and comprises

- Comminuting the plant material from which the oil is to be extracted
- Mixing the comminuted material with a carrier such as water
- Optionally blanching and deaerating the mixture
- Subjecting the mixture to a cell-bursting step by exposing the mixture to pressure variation
- Optionally introducing a malaxation step
- Separating the mixture into a solids and a liquid fraction
- Separating the liquid fraction into an aqueous and an oil fraction, which may be carried out in two stages[30]

A process for producing a high-grade food protein product has been disclosed in Parker et al. (1997).[31] The oilseeds are first conditioned to the right moisture content. Then they are "flash-sterilized" by heating for not more than 2 min, for instance, by immersing them in hot oil. Then they are expelled in a preheated screw press. This process raises the question of whether or not allowing the screw press to reach a temperature between 107°C and 132°C by feeding it with hot oilseeds and using the friction inside the press to raise the temperature further would infringe on the process.

Finally, I want to discuss a patent that discloses a process for defatting coconut meat. Normally, coconut meat is dried to prevent it from getting moldy and shipped as dry meat or copra. The moisture content should be <5%, which, given the oil content of some 65%, still amounts to 15% moisture on non-fat solids. At the oil mill, the copra is comminuted and flaked to open the cells; a first pressing yields oil and a cake with some 15% residual oil, which is then obtained by solvent extraction. In the process disclosed by Baensch (2008), the meat is not dried but grated and cooled to <15°C to solidify the coconut oil present in the meat. When this cold material is pressed, the solidified oil remains in the cake. This is then heated to melt the oil and pressed again. Residual oil can be obtained by washing the cake with water. A heat pump can be used to cool the grated meat, and presses and centrifugal separators can be used in the separation steps.

A process to produce coconut oil from fresh coconut milk has been disclosed by Khalid et al. (2010). They prepare the milk by squeezing the coconut meat at ambient temperature and then freeze the milk, which causes it to separate into water and an emulsion, keep it overnight, and then irradiate it with microwaves while controlling the temperature. The process can also be used for jatropha, oil palm fruits, and palm kernels.

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[30] Yes, this application also originates from an equipment manufacturer.

[31] The oilseeds are peanuts, which, given the location of the assignee (Atlanta), is not that surprising.

4.4 Enzymatic Pretreatment

Enzymes are gaining popularity and are being promoted for use in degumming and interesterification. Likewise, they attract some attention in oil milling. After all, if using enzymes means no hexane is involved, this might lower investment in the extraction plant and marketing departments might refer to the resulting oil as "natural," "biological," or "organic" while stressing the non-use of and non-exposure to solvents.[32]

As is only to be expected, early publications (Smith et al. 1993; Tano-Debrah and Ohta 1994, 1995; Hernandez et al. 2000) treating the enzyme-assisted production of vegetable oil originate mainly from academia, but there is also a patent application originating from industry (Laiho et al. 1991). It was pursued in Finland and Canada but allowed to lapse.

The process according to Laiho et al. (1991) sets out to retain the phosphatides in the aqueous phase by hydrolyzing them enzymatically so that the oil starts to form a separate layer that can be isolated by centrifuge. As expected, the oil obtained this way has a low phosphatide content in comparison with the oil obtained by solvent extraction, but the specification does not mention how much (or how little) oil was obtained by the process according to the invention.

An interesting patent aspect of this application is that its claims were amended before the application was published. Accordingly, the published application lists the original claims and then, on a subsequent page, the amended claims. It also comprises the Search Report listing four documents, each of which carries an "X" meaning "a document of particular relevance that destroys novelty and inventiveness"; this may well be the reason why the application was not pursued.

European Search Reports categorize the documents considered to pertain to the application being examined. Table 4.1 lists the various categories and their current definitions. The definitions used in early Search Reports used the same letters but were far less detailed. So according to Table 4.1, the X stands for lack of novelty and the Y for obvious. Those are the serious categories. Apart from the category, the Search Report also indicates which paragraphs in the cited document are considered to be relevant to which claim(s) in the application. They can pertain to only a few claims, and so even when the Report contains a number of Xs, not all need be lost.

In 2000, Öhmi Engineering applied for a patent (Hollien and Börner 2000) specifying the comminution of oilseeds to open the cells and liberate the enzymes and mixing the resulting flour or flakes with water to allow enzymes present in the oilseed to cause a range of different reactions to proceed. In the discussion of the prior art, the patent lists the need to purchase expensive enzymes and the long reaction times required as its disadvantages. However, the process according to the invention also has its disadvantages. It comprises drying the aqueous mash to a water content that is close to the water content of oilseeds. Given the water content of this mash

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[32] Given the presumed favorable connotation of the word "organic," I think industry has missed an opportunity by not highlighting the fact that *n*-hexane is organic rather than inorganic.

Table 4.1 Categories of documents cited in European Search Reports

A	Document defining the general state of the art which is not considered to be particularly relevant
E	Earlier document, but published on or after the international filing date
L	Document which may throw doubts in priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
O	Document referring to an oral disclosure use, exhibit or other means
P	Document published prior to the international filing date later than the priority date claimed
T	Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
X	Document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is taken alone
Y	Document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents, cush combination being obvious to a person skilled in the art
&	Document member of the same patent family

and the high latent heat of evaporation of water, this is an expensive step. Oil yield by pressing may be higher than without the enzymatic treatment but at 86% is far from ideal, and the application does not say anything about oil properties, especially peroxide value. The granted patent has not been maintained.

A patent that has been maintained and belongs to a family of 27 members is Maenz et al. (2000). It discloses an enzymatic process employing a phytase that converts phytates present in the oilseeds into inorganic phosphates. A chelating agent such as citric acid should preferably be added to remove the calcium ions bound to the phytates since these calcium phytates are much less susceptible to enzymatic hydrolysis than free phytic acid. According to the invention, the oilseeds are first comminuted and then slurried in a mixture of water and an organic solvent that constitutes 20–85% of the mixture. The invention increases the value of the meal, but given the amount of water used in the slurry, drying costs are also increased.

In a patent granted to Reverso (2000),[33] enzymes that are capable of breaking down the polysaccharides forming the integuments in which the oil is embedded are used to free the oil that is recovered mechanically without the use of solvents. The interesting aspect of this patent is that the enzymes are prepared *in situ* by inoculating the oilseed with "at least one microorganism selected from the group consisting of bacteria, fungi, hyphomycetes, and mixtures thereof." Accordingly, this patent discloses a way to avoid the purchase of expensive enzymes.

Since the inventor lives in Italy, it is not surprising that he sees an important application of his invention in the treatment of olive pomace. Similarly, he obtains the oil by using a two- or three-phase decanter and disposes of the solids as a fertilizer rather than as a feed ingredient. Accordingly, he does not dry the solids and thereby saves money.

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[33] There is only one equivalent, which is Italian.

Sharma et al. first treat rice bran (2001) with a commercial enzyme (Protizyme™), which is a mixture of various proteases and, in a second article (2002), describe the use of the same enzyme mixture to treat peanuts. In the case of rice bran oil, an enzyme cocktail consisting of the Protizyme™, an amylase, and a cellulase liberated the most oil. In the case of the peanuts, varying the process conditions led to an oil yield of 91%. The authors also compared this enzyme mix with other more or less pure enzymes and concluded that Protizyme™ was the most effective. The use of an amylolytic enzyme to digest peanuts and facilitate oil production by pressing and/or extraction has been disclosed in (Zhou and Huang 2009).

When plant seeds containing oil are comminuted, mixed with water and a lipase, and allowed to react, free fatty acids are formed (Mouloungui and Mechling 2004). They can be isolated from the resulting emulsion by extraction with an organic solvent such as an alcohol, an ester, an organic carbonate, or a ketone. The application led to a patent family of four members (AU, EP FR, WO). The Australian application was not pursued, and according to INPADOC, the European application is still being examined.[34] So more than 9 years after an application with a priority date of 4 September 2002 was filed, it is still not clear whether or not a patent will be granted.

The last patent application (Milke and Shaikh 2001)[35] I want to discuss discloses an enzymatic process to produce coconut oil. The specification is remarkable since it incorporates a long list of definitions. Almost every word in the claims is defined. The process itself uses about 2% of enzymes, preferably a hemicellulase, and the oil yield is less than 90%, which explains why interest in enzymatic oil production processes is, in fact, quite limited: They are too expensive. As will be explained in the next chapter, using enzymes to hydrolyze phosphatides can increase the oil yield; if that saving more than pays for the enzyme, it will be used. In the case of oil production, the oil yield decreases in comparison with the standard industrial process, so there is no economic incentive to start using enzymes. It is interesting to note that in the case of phospholipases, the enzyme manufacturers develop novel enzymes by genetic engineering and then apply for patents, whereas in the case of oil production, they do not.

That is to say, until recently. Danisco A/S,[36] which has taken over the enzyme producer Genencor, applied for a patent (Birschbach et al. 2008) disclosing a process to destabilize the emulsion that often results when comminuted oilseeds are extracted with water by contacting the emulsion with a phospholipase and/or a protease. The enzyme producer AB Enzymes GmbH[37] also applied for a patent (Köhler et al. 2010) claiming a process to recover oil from plant seeds in which the

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[34] According to the INPADOC Register, "Examination is in progress. *Database last updated on 06.12.2011.*"

[35] The applications published in Australia and Canada are deemed to have been withdrawn.

[36] In turn, Danisco has now been taken over by E.I. du Pont de Nemours and Company.

[37] This company was formerly Röhm GmbH. Together with MetallgesellschaftAG, it applied for the Enzymax® enzymatic degumming patent (Aalrust et al. 1992).

preferably dehulled seeds or press cake are sprayed with an enzyme solution before being pressed or extracted with a solvent. The latter application strikes me as defensive in that I interpret the long list of enzymes and their origins as the creation of prior art that aims at staving off the competition rather than protecting something useful.

4.5 Extraction Solvents

When writing about extraction solvents on an earlier occasion (Dijkstra 2007), I referred to a list of potential solvents and their properties (Johnson and Lusas 1983; Lusas et al. 1990). I also pointed out that not all solvents are allowed for contact with food products. That only applies to organic solvents, such as hexane (both *n*-hexane and isohexane), ethanol, isopropanol, acetone, acetic acid, and, of course, water and carbon dioxide. Even so, new solvents are regularly proposed.

I will therefore discuss the patents I have come across claiming the use of solvents other than hexane and carbon dioxide. I will discuss the use of hexane when dealing with the extraction process in the next section, and I will not discuss carbon dioxide because its use is too expensive for the tonnages processed in our industry. The patents claiming the use of carbon dioxide and/or supercritical conditions I came across originate from Nguyen et al. (1992), Peter and Brunner (1993), Rice (1994), Schulmeyr et al. (1994), Jameson (1996), Hiltunen and Vuorela (1998), Heidlas et al. (2005), Chordia and Martinez (2006), Bork and Lütge (2008), Garwood and Garwood (2008), Boisdon et al. (2008), and Donaldson and Quirin (2008).

In another patent listing Heidlas as first inventor (Heidlas et al. 1995),[38] it is argued that using carbon dioxide requires very high pressure ranges (>500 bar) and that using liquid propane is less costly and very effective when used at a pressure between 10 and 30 bar and a temperature between 10°C and 55°C. The propane may contain other alkanes, such as butane. In a later Degussa patent application (Wiesmüller and Pilz 2009),[39] a mixture of compressed C_2 to C_4 hydrocarbons is used to extract oil from pips and berries.

Several patents and patent applications disclose the use of propane or butane as extraction solvent. Benado (1991) discloses a continuous extraction process for vegetable matter, or preferably cereal bran, or preferably rice bran, with a normally gaseous hydrocarbon, or preferably propane. Another patent (Hebert et al. 1996) is also concerned with rice bran and also uses propane at a low temperature to avoid protein denaturation. The process concerned is a batch process, which may be the reason why the Canadian application (Hebert et al. 1997) has not been pursued.

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[38] This patent has been assigned to SKW Trostberg (Süddeutsche Kalkstickstoff Werke), whereas patent Heidlas et al. (2005), which has the same inventor, has been assigned to Degussa (Deutsche Gold- und Silber Scheideanstalt), a company that merged with SKW Trostberg in 2001.

[39] The US application writes Wiesmüller without umlaut mark.

In (Hall et al. 2003), butane is used to extract cocoa butter from cocoa liquor. Claim 33 specifies its scale of operation as at least 13,600 kg/day of cocoa liquor to produce (claim 34) at least 272 kg/h of defatted cocoa powder and 295 kg/h of cocoa butter. In Europe, the fat cannot be sold as cocoa butter since this name is reserved for fat that has been obtained by just pressing.

When propane and butane are used on a larger scale, it is predominantly for producing mineral oil from tar sands, but why not throw in some oilseeds for good measure (Haefele et al. 1999)? I will not go into detail but just mention a patent application (Darrell and Russell 2006) and the resulting patent (Phillips and Russell 2008) to highlight the confusion concerning the surname of the first inventor. In the PCT application, this was Darrell, but in the US patent, Darrell was the first given name and the surname was now Phillips. Things like that happen even with US citizens applying in the US through US agents; they can complicate searches.

Another patent using a liquid extraction solvent that is a gas under standard temperature and pressure is (Walters and Dodds 1999); it mentions butane in a dependent claim. It removes the solvent from the extraction residue by lowering the pressure to below the vapor pressure of the solvent at the prevailing temperature. The process is used not so much for extracting oil from oilseeds but rather to defat fried food products. Not surprisingly, this patent is cited in a later patent (Franke 2001b)[40] that also discloses the use of solvents that are normally gaseous and are therefore used at a temperature below 0°C to become liquid. It lists a vast range of solvents, including lower alkanes, sulfur dioxide, carbon dioxide, halogenated lower alkanes, ammonia, nitrogen, dimethyl ether, and so on, but in the examples, only isobutene is used.

The abstract of a "Process for removing oil from dairy food products" (Franke 1998b) reads, "A process for removing fats and oils from prepared animal-derived fried food products, particularly fried meat, poultry and fish products.…" – which rather contradicts the title. The claims are concerned with defatting cheese, a dairy product, and propane is the preferred extraction solvent. In fact, five patents (Franke 1994, 1998a, 1998b, 2001a, 2001b) stem from an application filed in 1991 and continued several times. This apparently may cause some confusion when editing individual patents and shows again that we should not believe everything we read.

A recently granted patent (EP 1 500 695 B1) discloses a process to remove potentially harmful compounds like cyanoglucosides from vegetable oil by washing the oil with alcohol. The application (Jackeschky 2005) also included a process in which the oilseeds were soaked in alcohol and then pressed to yield an oil that after filtration was washed further with alcohol, but this process did not survive examination.

Alcohol is also used in an Australian application (Anderson 2002a) disclosing a process to fractionate oilseeds into hulls, oil, protein flour, and fiber. When the wet seeds have been dehulled, they are ground in the presence of alcohol and the resulting slurry is allowed to settle. Oil rises and is obtained by decantation. In this respect,

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[40] This patent (Franke 2001b) has only been granted in the US.

the process is quite different from that disclosed in (Diosady et al. 1989). This patent[41] discloses a process in which the oilseeds are finely ground and mixed with a polar solvent such as alcohol to form a slurry that is then extracted with a non-polar solvent such as hexane. The oil is recovered by evaporating the non-polar solvent, and meal is recovered by forwarding the slurry containing the polar solvent to a filter, optionally washing the filter cake, and drying the cake. The reverse solvent order is used to prepare a vegetable protein concentrate,[42] as disclosed by Kellens and van Doosselaere (2009). Soybean flakes are first deoiled with hexane, the hexane is removed by washing with dry ethanol, and replacing this with wet ethanol causes the sugars to be extracted.

The Diosady process is a variant of an earlier patent (Rubin et al. 1984) in which the alcohol contained ammonia and that claimed a proteinaceous meal of reduced glucosinolate content and a high-quality triglyceride oil, both acceptable as food ingredients. That may be so, but neither process uses the advantage that alcohol dissolves oil when hot and that this solution forms two phases on cooling, which decreases the amount of solvent to be distilled (Youn and Wilpers 1981; Sullivan 1985). Moreover, alcohol has a much higher specific latent heat of evaporation than hexane, so desolventizing the marc requires more energy than when hexane is used. A more recent patent application (Cheryan 2007)[43] does not make use of the reduced solubility of oil in alcohol either but employs membrane filtration including nano-filtration to restrain an oil concentrate and pass a permeate of the ethanol solution.

Another patent that discloses an extraction solvent that dissolves oil when the temperature is between 35°C and 55°C but forms distinct oil and solvent layers on cooling to a temperature range of 15–25°C is (Kapila et al. 2003). This patent was published as Application US 2002/113227, which lists many more claims than the granted patent: 30 *versus* 1. In the application, hydrofluorohydrocarbons with the general formula $C_nH_{2n+2-x}F_x$, with $4<n<8$ and $1<x<18$, were claimed, but in the granted patent the only hydrofluorocarbon is decafluoropentane, which is added in an amount of 60–70% by volume of the total solvent to hexane. But then the application was continued in part and thus led to two further granted patents (US 6,793,951 and US 6,800,318), which both have 30 claims very much like the original application.

There are more patents claiming the use of fluorocarbons (Powell et al. 2001; Wilde 2005; Wilde et al. 2007), but they are for special products rather than for commodities. I read them with interest since the oldest one was assigned to ICI, my first industrial employer. The use of hydrofluoroethers of the general formula $C_nF_{2n+1}OC_mH_{2m+1}$ in

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[41] The text also provides a great historical survey of oilseed extraction processes, starting with the Bollmann extractor (1922) and the Hildebrand extractor (1934) and mentioning the rotary Blaw-Knox extractors (Karnofsky 1957) and many more recent extractors.

[42] I said that I was not going to discuss protein concentrates and isolates, but since I wrote this application myself, I make an exception.

[43] Also published as US Patent No. 7,767,836 B2.

extracting and fractionating fats has been disclosed by LeMaire et al. (2004). The examples show how karitene[44] can be removed from shea butter. In my opinion, karitene removal with acetone or by a dry fractionation is a simpler process.

Corn oil can be extracted by using a halogenated solvent that is preferably *n*-propylbromide (Faulconbridge et al. 2006). It claims a low energy usage and yes, the heat of evaporation of *n*-propyl bromide is only 30 kJ/mol, or 240 kJ/kg. This is low in comparison with *n*-hexane (340 kJ/kg) and especially alcohols like isopropanol (660 kJ/kg) or ethanol (840 kJ/kg). However, the miscella strength mentioned in the patent is only 1–2%, and this entails a large distillation volume. But then the same company applied for another patent (Wills 2004) that aims at drying solid material by replacing the water present with ethanol and then replacing the ethanol with a solvent having a lower heat of evaporation, such as *n*-propyl bromide. Rectifying the solvents takes up a lot of energy though.

Finally, two patents (Davis et al. 2006; Catchpole et al. 2007) originating from Australia and New Zealand, respectively, disclose the use of dimethyl ether as extraction solvent. This solvent has an atmospheric boiling point of –25°C, which facilitates desolventizing the marc. Because of this low boiling point, the extraction process is carried out under pressure, but this pressure is moderate (<10 bar).

The earlier patent application (Davis et al. 2006) was published on 8 June 2006, which is only a few days after the priority date (24 May 2006) of the later application (Catchpole et al. 2007); it can therefore not be regarded as prior art. So I wondered to what extent the granted claims of the later patent had been affected by the earlier application. They have not been since the earlier application was abandoned. The reason for this could well be the Search Report that mentions a patent application (WO 1999/043446) disclosing a process for cleaning and recycling solvents and the removal of oil from materials. This application mentions the use of dimethyl ether, for instance. The fact that the oil is a lubricant oil and that the material is an adsorbent used to clean garage floors does not disqualify this application from being regarded as prior art since the extraction process and the solvent recuperation steps are very similar indeed.

A rather weird patent application is (Chou and Chien 2007). It discloses a process of producing a solution of triglycerides in fatty acid alkyl esters by extracting an oil-bearing material with these esters. This is not entirely unexpected since the first inventor has also been mentioned in two earlier applications dealing with biodiesel production. The specification mentions that the esters can be at least partially removed from the oil solution by evaporation, but what to do with the ester–wet marc is not discussed at all. Given the low volatility of the alkyl esters, their recovery from the marc is far from straightforward.

Another pretty involatile extraction solvent is jojoba oil, a wax that can also be described as a fatty acid alkyl ester. According to Chaitman (2009),[45] jojoba oil can

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[44] Karitene is not a compound in the chemical sense but a mixture of unsaturated hydrocarbons present in crude shea butter, *Butyrospermum parkii,* now called *Vitellaria paradoxa.* This wild fat is called *beurre de karité* in French, hence the name karitene.

[45] The inventor lives in Hawaii, in the US, but the only application has been filed in Germany.

be used to extract ethereal oils. The extract is dissolved in hot alcohol and cooled so that the jojoba oil crystallizes and removal of the crystals leads to an alcoholic solution of said ethereal oil. It can be obtained in pure form by evaporation of the alcohol. The use of jojoba oil allows the ethereal oil or its solution to be called "biological" or "ecological." Again, recovery of the jojoba oil from the extraction residue is not discussed at all.

4.6 Solvent Extraction Processes[46]

In 2000, Johnson wrote an excellent review of solvent extraction processes, but surprisingly, he did not refer to any patents. The processes he reviewed have in common that all cell rupturing steps such as flaking, expanding, and screw pressing precede the extraction. Accordingly, insufficient cell rupturing cannot be remedied once the material has entered the extractor. The process disclosed by Coenen (1993)[47] differs in this respect in that it comprises a number of rotor–stator units in which the slurry of the material is comminuted while it is being extracted with a solvent.[48] Intermediate separation steps allow this material and the solvent to move countercurrently. As far as I can judge, the process has innate advantages, but nevertheless, it was apparently not adopted by industry; I can only wonder why. An extraction process for the wax present in the solid residue obtained from sugar cane juice does not require cell rupture but good mixing. An apparatus providing agitation in a direction that is perpendicular to the plug flow direction of the material being extracted has been disclosed in Fukuyo et al. (1999).

Food Sciences, Inc. is a company in Jennings, LA; it is interested in producing rice bran oil, and this interest has led to at least three US patents (Arendt and Langley 1995a, 1995b; Langley and Finelt 1997) and a whole range outside the US. Their specifications are a prime example of insufficient familiarity with the subject. The Background of the invention in Langley and Finelt (1997) starts as follows:

> "It is known that the best and easiest oilseed to process is soy bean. Rapeseed has also been processed on the kind of equipment used to process soy bean; however, it must be ground, cooked, and rolled into flakes to provide an extractable bed. Generally flakes can be run only at a much slower rate than soy beans."

Apparently, there are people in the US, a country that processes more soybeans than any other country, who do not know that these beans also require flaking. Similarly, claim 1 of Arendt and Langley (1995b) specifies, "A method for extracting

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[46] See also http://lipidlibrary.aocs.org/processing/solventextract/index.htm.

[47] Early applications in this family of eight applications were by Krupp GmbH, but later ones were by Dorr-Oliver Deutschland GmbH. However, from 1998 onward, no annuities were paid, and so the granted patent has mostly lapsed.

[48] The inventor also wrote a journal article (Coenen et al. 1989) about his process.

oil from oil-bearing grain materials or grain products … while the *bed of rice bran* is being moved horizontally … .” This bed has not been mentioned before at all, which is highly irregular.[49] The use of methyl acetate and ethyl acetate sounds impractical, and the process is not countercurrent and thus inefficient, so I think we can forget about the disclosures of Food Sciences, Inc.

A more useful disclosure has been made by Tydiks (1996). It concerns the use of a filter centrifuge to treat the solvent–wet marc before it is sent to the desolventizer. The filter centrifuge can be a so-called pusher centrifuge or a conical sieve centrifuge that is fitted with a co-rotating scroll.[50] The specification mentions that the solvent content of the marc can be reduced from 25–35% to 5–20%, or preferably 5–15%, or more preferably 5%; there is no example showing what can be attained, but my experience with the conical sieve centrifuge in fractionation (Maes and Dijkstra 1985)[51] gives me the impression that with a non-viscous liquid like miscella, values below 15% should be possible. This means not only that the amount of solvent that has to be evaporated in the desolventizer is halved, but also that the residual oil content of the meal is halved. Both effects constitute substantial savings. However, these savings should not be looked at in isolation since the possibility of reducing the solvent content of the marc can also be exploited by increasing the miscella strength and/or increasing the plant throughput. Similar but smaller savings are realized by the process disclosed by Kemper in 2007, who uses a screw press or a piston ram press and arrives at 20–21% residual solvent content after pressing the marc.

In my search for pertinent patents, I also came across two patents that originate from Russia: Kuznetsov et al. (2003) and Kusnetsov (2005). Both of these inventors have the given name Vitaly, both are named Nikolaevich after their respective fathers, and both live in Krasnodar. This might well lead to the conclusion that they are one and the same person and that the different spelling of their names stems from transcribing the Cyrillic into the Roman alphabet. When searching for names, this is something to guard against.

The older of the two patents is a PCT application in Russian. The claims are also in Russian, but the abstract is in a kind of English.[52] The application discloses a two-stage extraction starting with a preextraction in an immersion-type extractor followed by a vertical countercurrent extraction by superheated solvent vapor. A heating element has been provided to generate the superheated solvent vapor.

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[49] This raises the question of whether the patent concerned would qualify for a reissue ☺.

[50] The German text also mentions *Schwingzentrifugen,* so I went to the German Google to try and find out what type of equipment was meant by this. Lo and behold, I arrived at the main claim of Tydiks (1996) and a tentative translation into “oscillating centrifuge,” whatever that might be.

[51] In fact, Pieter Maes and I tried a whole range of centrifugal equipment, including decanters, pusher centrifuges, and basket centrifuges, before arriving at the conical sieve centrifuge with co-rotating scroll.

[52] In English, we normally talk about extracting oilseeds, but the abstract talks about extracting vegetable oils. In fact, this is more logical. We go to the dentist to have a tooth extracted and not to have our jaw extracted.

The other Russian patent (Kusnetsov 2005) is also a PCT application, but this one is in charming English,[53] and so I was able to study the description. The process involves a countercurrent extraction with boiling solvent. This causes some agitation of the material to be extracted, but since an Archimedean screw moves this forward, it is agitated anyway. Since boiling the solvent requires energy, the process strikes me as expensive, and it does not lend itself to the large scale of operation that is now common in Argentina or Brazil.

Improvements of large-scale, percolation-type extractors have been disclosed by Anderson (1998). They comprise a sprocket-driven continuous chain-link conveyor that has an upper run that moves the material to be extracted past sparging nozzles and a lower run that continuously cleans the collection chamber by scraping its bottom free of sedimentation and hazardous buildup. The material to be extracted is supported on a plurality of spaced-apart longitudinal members, a kind of slotted grid that retains solids but allows liquid to pass through.

In the same year, 1998, Kemper disclosed an improvement to a rotary immersion-type extractor. He locates both the lower thrust bearing that supports the axial shaft around which the baskets rotate and the central upper bearing outside the extractor housing, thus facilitating maintenance. The abstract of the patent also describes a hopper having an entry with a smaller cross-sectional area than the hopper exit, which allegedly prevents the agglomeration of solid material in the hopper, but none of the claims mentions such a hopper with improved discharge.

Solvent-assisted screw pressing has been disclosed by Smallridge and Teeter (2006). The solvent can be an organic solvent or carbon dioxide, and the application claims both the defatted biomass and the method of producing a defatted cake and an oil. The Search Report lists an article (Crowe et al. 2001) as pertinent prior art for the product claims and a patent (Rice 1994) for the process claims. Since the publication of this application, a patent (US 7,687,648; 30 March 2010) has been granted. It is interesting and instructive to see how the claims have been adapted during examination.

Just by comparing the two sets of claims, it is clear that the Examiner objected to the original expression of "less than 25 ppm phospholipids" when the element phosphorus was meant. Accordingly, the granted patent reads, "less than 50 parts per million phosphorous."[54] The original independent process claim (claim 16) listed only four consecutive steps, but the granted independent process claim became the main claim (claim 1) and now lists eight steps. It starts by prescribing dehulling.

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[53] It mentions raw stuff (raw material), concomitant substances (impurities), extractor of the submersible type (immersion extractor), overheated (superheated), sockets of input the solvent (solvent entry ports), drop catcher (demister?), etc. So it is possible to grasp more or less what is meant; finally discovering what is meant is fun, but it takes time. Is this translation the result of a mechanical translation? It could be since a spell checker would not find anything to correct. But translation programs always remind me of the instance when the expression "out of sight, out of mind" was translated into Russian by machine. The Russian output was then fed into a machine to be translated into English. Out came "invisible idiot."

[54] American authors tend to confuse phosphorus, the element, with phosphorous, which in Webster is defined as "of, relating to or containing phosphorus, esp. with a valence lower than in phosphoric compounds."

Then it lists the five process steps that were in the original independent product claim, whereby it narrows the scope by changing “solvent” to “organic solvent,” and finally, it concludes by listing the last step of the original process claim and formulating this as two steps specifying the separation of the oil and its recovery.

In the granted patent, the independent product claim has now become claim 6 and its scope has been reduced by specifying that the solvent is selected from the group consisting of non-toxic alcohols and gases and that the defatted biomass product is hexane-free. The granted patent also lists two more independent process claims (claims 9 and 10) that mention the PDI and the residual oil content of the defatted cake. Their main difference with what was claimed before is that they now also specify “the oil having an average of less than 100 ppm of phosphorous.”

The above illustrates how, on examination, claims can change quite considerably. Accordingly, it is always advisable to consult the granted patent when investigating whether or not an intended process or process modification infringes one or more patents held by the competition. Since patents are national, this investigation should include all countries in which patents have been granted. Applications indicate what might be granted and what warrants a close watch. Granted patents show what has been granted.

An application with claims that were less drastically adapted on examination is (Copeland et al. 2004),which led to the granted patent (Copeland et al. 2006). They disclose a process in which flaked soybeans are first extracted with an aqueous solution of citric acid to leach out the flatulence sugars and isoflavones, after which the wet extraction residue is extracted with acetone to remove the oil but leave the phosphatides in the extraction residue. Acetone is not only recovered but also produced by fermenting the aqueous solution of sugars, but they can also be fermented to form ethanol. Two solvents can be used; the first one is acetone since it is miscible with water and can “dry” the wet extraction residue, and the second one can be a hydrocarbon like hexane.

This patent (Copeland et al. 2006) allows me to discuss a patent concept that is called “unity of invention.” Say you have invented a process and would like patent protection for this process. An application is drafted in which the invention is disclosed and a number of examples illustrate how it works. As usual, the invention is only concerned with a single link in a whole chain of process steps, and although an essential link, you would like to broaden your protection to include as many other links as possible. The concept of “unity of invention” prescribes that what you claim must be related to the actual inventive process. So if your process involves a catalyst that is water-sensitive, the drying step is certainly an important aspect of your process and you can therefore include it in the specification, examples, and claims without losing unity of invention.

If this drying step happens to be an invention in its own right, you can include it in the specification dealing with the water-sensitive catalyst since drying is essential to the use of this catalyst. You can also devote a separate patent application and specification to the drying step since it is also an invention. You can also do both and include the drying step in the specification disclosing the catalyst and file another application for the drying step, but you must take care to file the applications in such a way that they cannot be regarded as prior art for each other.

Coming back to Copeland et al. (2006), claiming that the aqueous sugar solution resulting from the process according to the invention can be used in a fermentation process to produce acetone used in the extraction process according to the invention certainly does not violate the concept of unity of invention. However, claiming that this aqueous sugar solution can also be used in a fermentation process to produce ethanol strikes me as being outside the inventive concept; apparently, the Examiner held a different opinion.

Another application, (Tysinger 2005), which has been granted as US 7,579,492, is also concerned with a two-stage extraction. Whereas Copeland et al. (2006) first extracted sugars and isoflavones and then extracted oil, Tysinger extracts only oil but does this in two stages. The first stage can be either mechanical or by using a solvent, and the second one always employs a solvent. The oil resulting from this second stage is considered to be inferior and therefore interesterified to produce biodiesel.

On examination, the number of claims in (Tysinger 2005) was reduced from 23 to 10. Original claim 7 (“The process of claim 1, wherein oil is extracted from said soybeans by heating said soybeans to at least 300°F, crushing said soybeans, and mechanically pressing said soybeans”) was not accepted in view of Seaman and Stidham (1993), who also heat soybeans to 235–350°F and partially remove oil to arrive at a protein meal with a bypass value in the range of 55–65%.

4.7 Solvent Recovery Processes[55]

Solvent extraction processes generate two product streams: One is a miscella, which is a solution of oil in the solvent used to extract the oil. The oil content of the miscella varies but is usually around 30% by weight. The miscella has to be separated in solvent to be recycled and crude oil, but surprisingly, little has been published about solvent recovery from miscella. The apparatus disclosed by Weber (2000) is the only one. The other product stream is the solvent–wet extraction residue or marc. Again, the solvent content of the marc varies, but in general, it is also close to 30% by weight. The marc has to be separated: into solvent to be recycled and meal.

Both oil and meal require further treatment in that the crude oil is generally water degummed and the meal may be toasted to denature antinutritional factors and control the solubility of the meal protein. In addition, the water content of the meal has to be controlled within narrow limits. Exceeding the upper limit would cause mold to grow on the meal, and selling meal with less water than allowed by the lower limit of the meal specification amounts to giving money away.

An apparatus used to treat the marc and the ensuing meal is a DTDC, which stands for “desolventizer, toaster, dryer, cooler” (Schumacher 1986). It consists of a large cylindrical vessel fitted with superimposed decks around a central shaft that rotates the agitators that move the material across the decks. The decks have holes connected to chutes that allow the material to move to a deck below. Marc entering

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[55] See also http://lipidlibrary.aocs.org/processing/desolvent/index.htm.

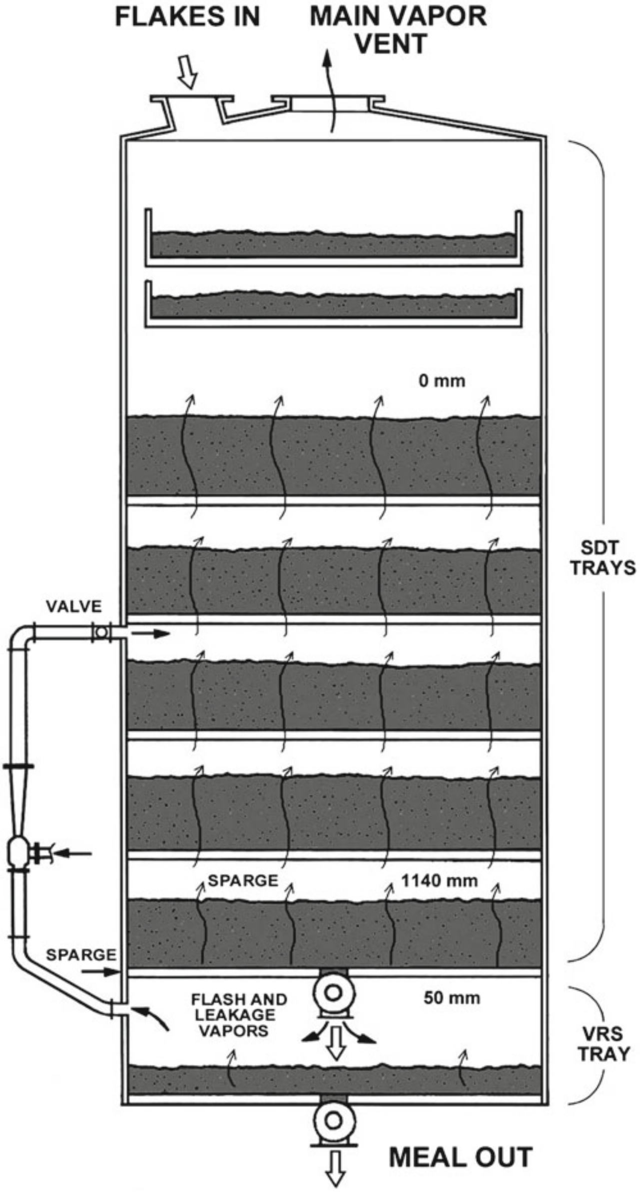

Fig. 4.2 Desolventiser with vapor recovery system (Anderson 2003)

the apparatus will have a temperature of some 57°C, which is close to the extraction temperature or just below the hexane boiling point. On entry, the agitator will spread the marc evenly over the uppermost deck. This is heated indirectly with steam so that some hexane will evaporate. More hexane will evaporate on the deck below that is also heated indirectly with steam. Figure 4.2 shows how this hexane will move upward around the indirectly heated deck and through the gap between these decks and the desolventizer shell, and leave the apparatus through a duct at the top.

According to Kratochwill (1997), a desolventizer with superimposed decks has several disadvantages. It has not been designed to handle abrasive solids that "would destroy a typical desolventizing unit equipped with sweep arms." In addition, the arms and paddles leave material on the decks, causing isolated solids to burn and/or be ground or broken up. Accordingly, Kratochwill discloses a desolventizer in which a superimposed series of "chain type conveyors having spaced wiper paddles over the length thereof" transport the material to be desolventized over a stack of heated decks. Each conveyor is provided with an upper deck and a lower deck, both of which are heated with steam.

According to Anderson et al. (2004), the apparatus described above (Kratochwill 1997) has the disadvantage that the temperature during desolventizing is sufficiently high to denature the protein in the meal. Accordingly, his three-stage desolventizer has a first stage that operates at reduced pressure and where most of the solvent is evaporated. The residual solvent is removed in the second and third stages of the apparatus by stripping with an inert gas such as nitrogen. The apparatus has been developed for the removal of butane ("a gas, well known as the fuel for backyard grills around the country") from cocoa powder, but as usual, its application is not limited to this instance.

The material leaving the indirectly heated decks of the DTDC will still contain some hexane. This is evaporated by treating this material with live steam on lower decks in a countercurrent manner. This steam condenses onto the material and raises its temperature to eventually some 107°C, where it is toasted and causes residual hexane to evaporate (Kemper 2000). To effect the countercurrent stripping, the decks extend to the deodorizer wall (see Fig. 4.2) and have holes in accordance with Anderson (1999) or spaced bar members in accordance with Kemper and Farmer (1999). Superheated steam is sparged from underneath the lowest deck.

Because the sparging steam condenses on the material, its moisture content has to be lowered in the drying section of the DTDC. Air is used to dry the material and cool it at the same time. Accordingly, a rotary valve is used to transfer the material from the last sparging tray to the drying/cooling section. This valve prevents the air from entering the upper, hexane-containing sections of the DTDC. To facilitate the removal of the last traces of hexane, a flash chamber that is kept at sub-atmospheric pressure may be inserted between the last sparging tray and the drying/cooling section (Anderson 2001, 2004a).[56] Two rotary valves (54) and (58) are required to separate the reduced-pressure flash chamber (56) from the desolventizing section and the drying section, respectively. Vapor extracted from the flash chamber is released into the desolventizing section as illustrated in Fig. 4.2, which has been taken from Anderson (2003).

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[56] During a Short Course held in Kuala Lumpur on 5–6 March 2010, D. Anderson of CPM-Crown Iron Works recommended this system especially for the desolventization of palm kernel meal.

Patent application (van Doosselaere 2003) discloses a similar system, but it is deemed to have been withdrawn. Another European application by Desmet Ballestra Engineering (Van Damme 2009) is also deemed to have been withdrawn as such but is being pursued in the United States, Argentina, Brazil, Germany, and the United Kingdom. Looking at the legal status of the application in the UK (GB 2 451 577) shows that this application has been used to obtain a patent in the Hong Kong Special Administrative region. The Hong Kong Patents Registry grants patents without examining them provided they originate from China, the UK, and Europe, provided the European patent designated the UK and provided a request to register the application in Hong Kong has been made within 6 months after its publication.

The application itself (Van Damme 2009) is concerned with equipment that permits a subatmospheric pressure in the desolventizer to be maintained by compacting the material to be desolventized in an extruder on entry and exit by formation of a gas-impermeable plug. This subatmospheric pressure encourages the hexane to evaporate. Another way to encourage evaporation is by stripping.

One way of stripping is to supply the stripping medium as a low-boiling liquid that is then allowed to evaporate. That is the principle of the desolventizing process disclosed by Wills (2003). In this process, the hexane present in the marc is first diluted by mixing the marc with a lower-boiling hydrocarbon such as butane. When this mixture is then separated in a decanter, the solids fraction has a much reduced hexane content. When the butane is then removed by evaporation, the butane vapor will entrain the hexane still present in the solids fraction and thus cause the residual hexane content to be very low indeed. However, the process not only entails evaporating and condensing all the hexane present in the marc, but in addition, the butane also has to be evaporated and condensed since the liquid fraction separated by the decanter has to be subjected to a fractional distillation. Because of the low desolventizing temperatures in this process, it may well be highly suited for the production of white flakes.

Another patent application by Crown Iron Works (Anderson 2004b) is also concerned with desolventizing. Since it has been applied for in China, all I have read about it is the abstract as provided by Espacenet. The system comprises a vacuum system and presumably two desolventizer units in series that are separated by "pressure transit cabins," presumably a kind of device as disclosed in (Van Damme 2009). The interesting thing about this application is that the patent family also lists HK1063482. It thereby illustrates that a Chinese application publication can also serve as a means to register a patent in Hong Kong.

The vapors leaving the desolventizer consist mainly of hexane. The latent heat in this hexane vapor is used to evaporate hexane present in the miscella, and to save energy, a multiple effect evaporator is generally used to recover the crude oil from the miscella. This means that the savings resulting from the use of membrane technology (Raman et al. 1996) are, in fact, overstated. A similar overstatement was made in Darvishmanesh et al. (2011), which caused me to write a Letter to the Editor of the *JAOCS,* which is in print at the time of this writing.

It is not clear to what extent the savings claimed in an extraction process (Prevost et al. 1998) that uses propane and/or butane as extraction solvent and a ceramic membrane to recover the solvent from the miscella are realistic since the cost of operating under pressure also has to be taken into account. The granted patent (Prevost et al. 1998) has not been maintained, and in Europe its equivalent (EP 0 942 657) has been deemed to be withdrawn. On the other hand, using a membrane to separate a solvent with a high specific heat of evaporation like isopropanol (IPA) from oil or to dry the IPA/water azeotrope (Kőseoğlu et al. 1995) may well be or become cost-effective.

4.8 Production of Cocoa Butter

So far, the sections in this chapter have focused on processes, but the present section will focus on a starting material – the cocoa bean – and discuss the production of cocoa butter. This production makes use of several of the processes discussed earlier, but it is nevertheless special because cocoa butter is an expensive product and subject to a whole range of rules and regulations.

Cocoa trees grow pods that contain some 20 to 40 cocoa beans. After having been harvested, they may be fermented before being dried and shipped to the cocoa mill. At the mill, the beans are roasted to loosen the shell from the nibs.[57] The shells are separated from the nibs by winnowing, and then the nibs, which contain some 50–58% of cocoa butter, are ground and milled to form cocoa liquor. This can be separated by hydraulic or screw pressing into cocoa butter and cocoa cake that still contains some (10–12%) cocoa butter. Grinding the cake produces cocoa powder. The color and flavor of this powder can be altered by the alkalizing[58] process, which involves adding an alkali (sodium or potassium carbonate) to the beans, nibs, liquor, or cake.

Cocoa beans also contain polyphenols. According to US Patent No. 5,554,645, polyphenol extracts that contain procyanidins have significant utility as anticancer or antineoplastic agents. Accordingly, Mars, Inc. filed a patent application (no. 08/709,406) on 6 September 1996 disclosing a process for producing cocoa cake with a high polyphenol content. This application led to US Patent No. 6,015,913 (Kealey et al. 2000).

Parent continuity data

Description	Parent number	Parent filing or 371(c) date	Parent status	Patent number
This application is a continuation of	11/129,892	05-16-2005	Abandoned	–
is a division of	10/648,131	08-26-2003	Patented	6,905,715
is a division of	09/841,925	04-25-2001	–	–
is a continuation of	09/441,302	11-16-1999	Abandoned	–
is a division of	08/709,406	09-06-1996	Patented	6,015,913

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[57] This jargon shows that the cocoa world is a world of its own. Soybeans are dried and dehulled before being separated into hulls and meats or cotyledons. Cocoa beans are roasted and winnowed before being separated into shells and nibs.

[58] This process is also referred to as “dutching.” It was developed by the Dutchman Coenraad van Houten in 1828.

The table on the previous page is what you see when you go to the USPTO website, go to Patents, and click on *Check status*, click on *Public PAIR* in the next window, type in the two words that are shown in funny letters, then select application number, type in 11928509, and go to the *Continuity Data* tab. It shows that application 09/841,925 apparently did not lead to a patent, but it did: US Patent No. 6,737,088 (Kealey et al. 2004) corresponds to this application number.

Clicking the Continuity Data tab for the earliest application (08/709,406 of 6 September 1996) shows a substantial number of offspring, as shown below:

Child continuity data

09/841,925 filed on 04-25-2001 which is Click Here claims the benefit of 08/709,406
09/981,529 filed on 10-16-2001 which is Patented claims the benefit of 08/709,406
10/636,931 filed on 08-07-2003 which is Patented claims the benefit of 08/709,406
11/926,951 filed on 10-29-2007 which is Abandoned claims the benefit of 08/709,406
11/928,509 filed on 10-30-2007 which is Pending claims the benefit of 08/709,406
09/440,898 filed on 11-16-1999 which is Abandoned claims the benefit of 08/709,406
09/441,302 filed on 11-16-1999 which is Abandoned claims the benefit of 08/709,406
09/470,394 filed on 12-22-1999 which is Patented claims the benefit of 08/709,406
09/764,193 filed on 01-17-2001 which is Patented claims the benefit of 08/709,406
PCT/US97/15893 filed on 09-08-1997 which is Published claims the benefit of 08/709,406
09/992,932 filed on 11-05-2001 which is Patented claims the benefit of 08/709,406
10/011,068 filed on 11-08-2001 which is Patented claims the benefit of 08/709,406
10/037,079 filed on 11-09-2001 which is Patented claims the benefit of 08/709,406
10/648,131 filed on 08-26-2003 which is Patented claims the benefit of 08/709,406
11/129,892 filed on 05-16-2005 which is Abandoned claims the benefit of 08/709,406
11/745,766 filed on 05-08-2007 which is Abandoned claims the benefit of 08/709,406

I will not discuss the above family tree in detail. I only want to show that consulting the USPTO website can provide valuable background data on how US patents and applications are related. This could be especially valuable for non-US readers since relationships such as “continuations in part” and “divisions” are foreign to them.

Returning now to the technical aspects of the disclosures in Kealey et al. (2000, 2004, 2005), they turn out not to be very remarkable and they are limited to controlling the internal bean temperature to 100–110°C during the roasting stage, during which the shells are loosened from the nibs.

Another family of related patents concerned with cocoa butter has been granted to Cargill, Inc.: (Purtle and Gusek, 2000) and (Purtle et al., 2002, 2003, 2010). They are concerned with the solvent extraction of cocoa liquor with propane and butane. This leads to much lower (<0.5%) residual fat contents than pressing the cocoa liquor. For the separation of the cocoa solids from the miscella, a belt filter may be used on which the filter cake can also be washed to further reduce residual cocoa butter. In another embodiment, a decanter is used for the solid/liquid separation, and then the solids are mixed with fresh solvent and again separated in a decanter.

Centrifugal separation is also used in the process disclosed by Wilke (1993). He mixes cocoa liquor with water and then separates the mixture into three streams: molten cocoa butter that can be further washed with water to isolate theobromine; an aqueous wash liquor containing some of the off-taste compounds; and a heavy phase containing the cocoa solids and some 30% water. This water can be removed in a vacuum drum dryer or a fluidized bed dryer.

I had never heard of cupuassu butter. However, the Latin name (*Theobroma grandiflorum*) shows it to be akin to cocoa butter, and the fatty acid composition is close to that of shea butter. It is therefore also called "the Amazon's shea butter." It can be used as a confectionery fat and also has cosmetic applications. According to Nagasawa and Numata (2002), it is produced by fermenting the cupuaçu[59] seeds to get the beans, which can then be roasted, threshed, and crushed. Another way of shelling the beans is to treat them with hot water or live steam, cut the shells, and take out the kernel, which can then be roasted and crushed. The crude cupuassu oil can be pressed to arrive at a purified product.

4.9 Miscellaneous Processes

A patent applied for by Lesieur (Triomphe and Declercq 2009) discloses a process to produce an oil with an agreeable taste. The process comprises mixing the oilseeds with common kitchen salt and roasting ($140°\text{C} < T < 160°\text{C}$) the mixture before expelling the oil in a press. Despite the increase in non-oil solids in the press cake, the oil yield increases as a result of this pretreatment.[60] The value added to the oil should compensate for the fact that its high salt content will make the resulting meal pretty useless as a feed ingredient.[61]

A salt (preferably sodium metabisulfite) is also used to stabilize rice bran (Wells and Belcher 2000) by inactivating the lipase and other enzymes present in the bran. Perhaps it is simpler to use hydrochloric acid for this purpose (Prabhakar and Venkatesh 1986). The salt can be added to the rice grain prior to, during, or after milling. The patent mentions that the defatted bran is desolventized under gentle heating with steam, yielding "a defatted bran with an oil content of less than 1%" but does not reveal in what application it can be used.

A patent application I tend to regard as a waste of money is (Vincent and Comis 2010). Its main claim specifies an oil having a low moisture content and a low peroxide value. Surely, the literature reports a whole number of such oils that thereby constitute prior art. The application also specifies that the oil should be prepared in

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[59] This is the Portuguese spelling of the plant.

[60] This reminds me of a patent (McClain 1951) that discloses the use of common salt as a filter aid in the winterization of sunflower seed oil. This also led to a remarkably low oil retention in the filter cake and thus a wax with a relatively low oil content (P.J.A. Maes, personal communication, 1997).

[61] A potential application I would like to investigate is fish feed pellets since they are scattered into the water, which may leach out the salt from the pellets before the fish start eating them.

the substantial absence of oxygen and light, which are redefined in a subsequent claim as reactive gases and predetermined wavelengths of electromagnetic radiation, respectively; exposing the oil to electrical currents should also be prevented.

And what about a granted patent (Quear 2001) that discloses an oil purification process comprising maintaining the oil at a temperature below 10°C, heating the oil to a temperature sufficient to provide an amount of substantially clarified oil, and drawing off the clarified oil? That is exactly what is being done during the winterization of sunflower seed oil. The oil is cooled to cause the wax to crystallize. Then the oil is heated to reduce its viscosity before being centrifuged or filtered. So the patent should not have been granted. In addition, its specification betrays a total lack of understanding of edible oil processing. After having described how crude oil is produced by screw pressing, the specification reports that it is refined by using a solvent extraction process in which the crude oil is extracted with an organic solvent, for example, a mixture of hexanes.

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Chapter 5
Degumming

5.1 State of the Art in 1990

> *To all whom it may concern:*
>
> Be it known that I, FRANCIS M. TURNER, a citizen of the United States of America, residing at New York city, county and State of New York, have invented certain new and useful Improvements in Processes of Purifying Oleaginous Substances, of which the following is a full, clear and exact description.

As far as I am aware, this is the publication (Turner 1923) with the earliest priority date[1] describing the water degumming process. It precedes the better-known Bollmann patent (1923) disclosing a process in which steam is fed into a miscella evaporation residue and the resulting lecithin is isolated from the oil.

At that time (1923), the chemical nature of the gums was not yet known. Turner talks about "mucilaginous or albuminous matter"; Bollmann talks about "lecithin" with a phosphorus content of 3.8–3.9%. Twenty-five years later, Boekenoogen (1948) still noted a confusion but suggested that the gums consist of phospholipids, only one of which is phosphatidylcholine, or lecithin. Then in 1960, Nielsen made a distinction between hydratable phosphatides[2] and non-hydratable phosphatides (NHP). In 1971, Hvolby showed that the atomic ratio of the sum of the calcium and magnesium content of water degummed oil and its phosphorus content is always less than unity; he concluded that the NHP consist mainly of calcium and magnesium salts of phosphatidic acid (PA). When studying degumming, I concluded (Dijkstra 1993) that in addition to these PA salts, NHP also contain variable amounts of free phosphatidylethanolamine (PE).

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[1] The priority date of the Turner patent is the date the application was filed: 6 March 1920. The German Bollmann patent was applied for on 25 June 1921, at which time the Turner patent had not yet been published. So two inventors made the same invention independently of each other. Actually, this happens quite frequently.

[2] In the literature, the words "phosphatides" and "phospholipids" are often used interchangeably. I prefer to regard phosphatides as a group of compounds within the phospholipids that also comprise phosphoglycolipids and sphingophospholipids, etc.

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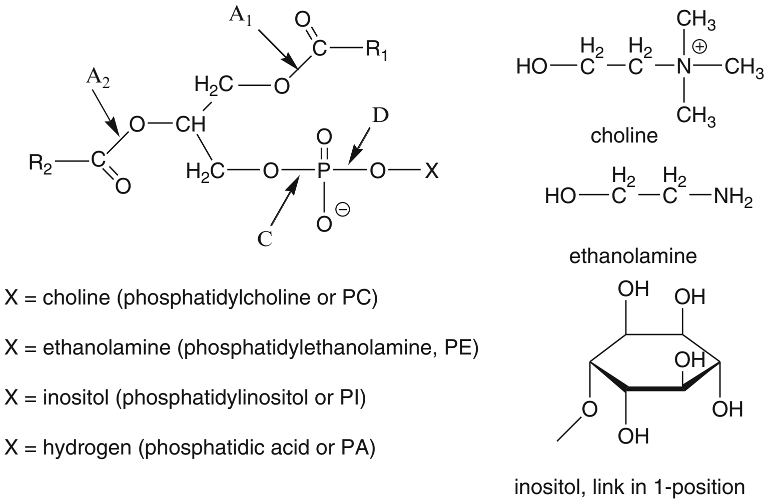

X = choline (phosphatidylcholine or PC)

X = ethanolamine (phosphatidylethanolamine, PE)

X = inositol (phosphatidylinositol or PI)

X = hydrogen (phosphatidic acid or PA)

Fig. 5.1 Chemical structures of phosphatides and their substituent groups showing the points of attack by various phospholipase enzymes

Figure 5.1 shows the chemical structure of the phosphatides and their substituents. The letters by the arrows indicate which phospholipase enzyme catalyzes the hydrolysis of which bond. The behavior of the most common phosphatides with respect to degumming reactions has been summarized ahead. These reactions include enzyme-catalyzed hydrolysis, although in 1990 these reactions were not yet used industrially.

- *Phosphatidylcholine* (PC). For steric reasons, the bulky trimethylamino group prevents the formation of an internal salt with the phosphate group. Consequently, the positive charge is always isolated, which may well cause PC to be hydratable at all pH values. At pH > 5, the phosphate group will dissociate so that PC will have a negative charge at the phosphate group in addition to the positive charge at the quaternary amino group. At pH < 3, the PC molecule only has a positive charge. PC is hydrolyzed by phospholipase A_1, A_2, and lipid acyltransferase (LAT) under formation of lysophosphatidylcholine (LPC) and free fatty acids. Under the influence of phospholipase C[3] (PLC), it forms diglycerides and choline phosphate.
- *Phosphatidylethanolamine* (PE). Like PC, PE has just a positive charge at pH < 3 and a positive and a negative charge at pH > 5. However, unlike PC, it loses its positive charge at pH > 9. PE can form an internal salt with a six-atom ring between the dissociated phosphate group and the protonated amino group; this salt has no net charge and may therefore be poorly hydratable. PE is hydrolyzed by phospholipase A_1 and A_2 and by LAT under formation of

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[3] The phospholipase C referred to is the Purifine® enzyme (recently acquired by DSM), which is the only PLC on the market at the time of this writing. It is specific to PC and PE.

lysophosphatidylethanolamine (LPE); PLC is able to hydrolyze PE to diglycerides and ethanolamine phosphate.

- *Phosphatidylinositol* (PI). At a $\text{pH} > 5$, the phosphate group in PI dissociates and provides the molecule with a negative charge. At lower pH values, PI has no net charge but is still hydratable because of the five free hydroxyl groups in the inositol moiety.[4] The enzymes PLA_1, PLA_2, and LAT catalyze the hydrolysis of fatty acid ester bonds in PI and cause lysophosphatidylinositol (LPI) and fatty acids to be formed. The PLC enzyme does not affect PI. So when an oil containing PI is treated with an aqueous PLC solution, the PI is just hydrated but not hydrolyzed.
- *Phosphatidic acid* (PA). The free acid has a pK_{a1} value of 3.8 and a pK_{a2} value of 8.6 (Abramson et al. 1964). During water degumming, PA will therefore have a single negative charge that makes it hydratable. During acid degumming, the pH will be below the pK_{a1} value, so that the PA will be hardly dissociated and thus poorly hydratable. That is why the acid refining process raises the pH to just above this pK_{a1} value by partially neutralizing the degumming acid with caustic soda. At neutral pH, PA is hydratable, as demonstrated by the presence of PA in lecithin, where it is present as the free acid or a potassium salt. PA is hydrolyzed by PLA_1, PLA_2 and LAT under formation of lysophosphatidic acid (LPA) and free fatty acids; it is not hydrolyzed by PLC.
- *Non-hydratable phosphatides* (NHP). They consist mainly of the calcium and magnesium salts of phosphatidic acid and some free PE.[5] They are oil-soluble and show hardly any affinity for the oil/water interface in a W/O emulsion. Removing these NHP from oil involves decomposing these salts with an acid that is stronger than PA itself and binding the metal ions originating from the NHP to prevent the decomposition reverting when the pH is raised. In practice, citric acid and phosphoric acid are used for this purpose since they are also food-grade. As will be demonstrated ahead, enzymes hardly cause any NHP hydrolysis under industrial conditions since this reaction is too slow to get underway during the relatively short period that the dispersion of the aqueous enzyme solution in the oil to be degummed is sufficiently fine for the reaction not to be diffusion-controlled.

With respect to degumming processes in industrial use in 1990, water degumming was used extensively to produce lecithin and prevent tank deposits during transport and storage. Lecithin production was limited to water degumming crude oil obtained from soybeans, which at that time had not yet been genetically modified. Once GMO beans came onto the market, other seed oils such as sunflower seed oil

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[4] I therefore disagree with the statement on page 8 in Dayton and dos Santos (2008) that “both PA and PI are non-hydratable phosphatides that remain in oil after water degumming.” When analyzing the phosphatides present in water degummed oil, I did not find any PI (Dijkstra 1993).

[5] The literature often refers to NHP as calcium and magnesium salts of PA and PE, but on an atomic basis $(\text{Ca}+\text{Mg}) < \text{P}$; this makes it likely that the PE is free. Besides, what would the structure of the calcium salt of PE be like?

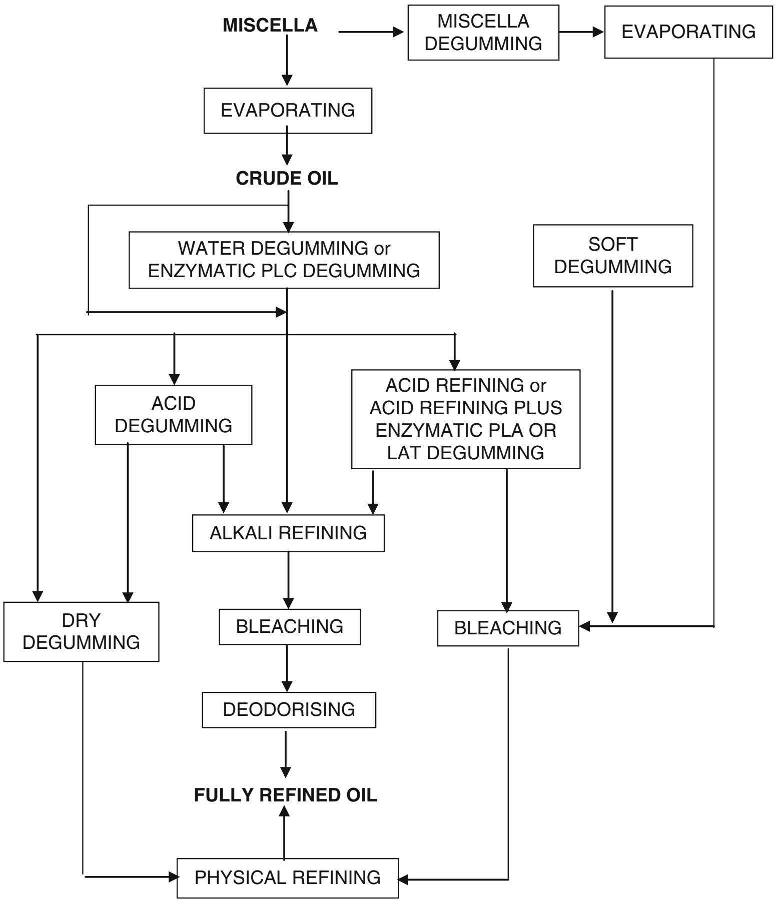

Fig. 5.2 Flow diagram representing the various refining routes

started to be used to produce lecithin for food applications for markets that were felt to be averse to anything reeking of GMO. In addition to the water degumming process, the dry degumming process (Sullivan 1978) was used more and more intensively to prepare palm oil, lauric oils, and tallow for physical refining.

Water degumming is applied to crude oils in the oil mill after solvent removal. However, according to Saft and Heilmann (2002), it is also possible to water degum the crude oil when it still contains some solvent, that is, after the bulk of the solvent has been removed and before the residual solvent is removed by steam stripping. The application has only been filed in Germany, and according to INPADOC, it is still under examination.

In 1990, Unilever was still operating its oil mills and refineries, and several of these employed the Superdegumming process (Ringers and Segers 1977; Segers 1982). In Fig. 5.2, this process has been denoted as ACID DEGUMMING. The process can use either crude oil or water degummed oil as feed, but since the guaranteed maximum level of residual phosphorus is 30 ppm P, Fig. 5.2 indicates that acid degummed oil is not a suitable starting material for physical refining. It needs an additional gum removal step, which, according to the figure, can be DRY DEGUMMING or ALKALI REFINING. To deal with this limitation, Unilever developed the Unidegumming process (Van de Sande et al. 1994),[6] which is, in fact, an acid refining step added on to the acid degumming process.

Unilever tried to license its Superdegumming process, but when offered a license, the Vandemoortele board considered the royalties Unilever was asking to be prohibitive. Later, when Unilever sold its refineries, it also "sold" licenses for the degumming processes operating in these refineries. However, these royalties showed the Vandemoortele board that the degumming process my department was working on could be more valuable than originally felt. This process became known as the Total Degumming Process (Dijkstra and Van Opstal 1989), or TOP according to its Dutch acronym, *Totaal Ontslijmingsproces*. For prior art reasons (Alexander 1980), I had to limit the first TOP patent (Dijkstra and Van Opstal 1987) to water degummed oils, but I could extend the scope of protection by including water degummed oil in the second TOP patent (Van Opstal et al. 1990),which describes the recycling of the gum phase leaving the second separator (Dijkstra 1993).

This was the process Vandemoortele used internally in its new refinery in Sète and subsequently in the refinery in Riesa, which it purchased from the Treuhand. It is also the process I explained in 1989 in oral presentations in Angers and Münster and on posters in Cincinnati, Gothenburg, and Maastricht. As a result, a TOP license was sold to Ölmühle Bruck, Austria, which was an independent oil mill at the time[7] and used the TOP degummed oil it did not sell to outside refineries for on-site biodiesel production. No more licenses were sold[8] until Vandemoortele sold its refineries and transferred the TOP patent rights to Westfalia Separator, Oelde. This company has installed several TOP lines, and at least five more have been installed by an Austrian company selling biodiesel plants (K-P Eickhoff, personal communication, 2008).

Acid refining was also used by Ölmühle Bröckelmann in Hamm, Germany, and because an infringement of the first TOPpatent was suspected, legal action was started. This was not pursued when Vandemoortele sold its refineries. Another company practicing acid refining is Bunge, the current owner of the Martfü site in

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[6] I discuss this Unidegumming patent in the introduction since the European application (Van de Sande and Segers 1989) dates from before 1990. The Unidegumming patent family consists of 28 patents, so it is not surprising that Unilever was seriously concerned when I opposed their European patent after it had been granted. This opposition caused the patent to be amended, but in the meantime, Unilever had also filed a divisional application that resulted in another Unidegumming patent (Van de Sande and Segers 1993) that belongs to another family of 28 members. This must have cost Unilever a pretty penny.

[7] Ölmühle Bruck changed hands, and when Bunge took it over, this company introduced its own degumming process (Rohdenburg et al. 1993).

[8] Vandemoortele regarded licensing as a commercial operation, and so a trader, whose regular job it was to buy oilseeds at the futures market, was told to sell TOP licenses when he had some spare time. No further licenses were sold.

Hungary where the Krupp acid refining process (Rohdenburg et al. 1993) was developed; in the literature, this Krupp process is also referred to as UF degumming. Contractors such as Alfa Laval and De Smet-Ballestra also offer acid refining processes; they are referred to as "special degumming."

5.2 Chemical Degumming Processes

The first patent I want to discuss under this heading is an application that led to a family of 21 applications and granted patents, among which is the US equivalent (Jamil et al. 2000). They concern the process that became known as the SOFT degumming process (Choukri et al. 2001; Deffense 1996)[9]. In this process, the NHP are decomposed by mixing the oil to be degummed with an aqueous solution of EDTA (ethylenediamine tetraacetic acid). To facilitate contact between the oil and the aqueous degumming agent, the use of an emulsifier – in practice, this is sodium lauryl sulfate – is mandatory because it is mentioned in the main claim. Consequently, Deffense (2002) could distantiate himself from the patent (Jamil et al. 2000) assigned to his former employer[10] when he found that the degumming process also works without an emulsifier.

For the process to work, the reaction between the EDTA and the NHP must reach near completion. This reaction takes place at the oil/water interface, which implies that a large interfacial area increases the rate of reaction. Such a large interface results from a fine dispersion of the aqueous phase in the oil, which also has the advantage of reducing the distance over which NHP molecules have to diffuse before they reach the interface, thus shortening the time required to reach the interface. The approach by Jamil et al. (2000) is to create a reasonably stable emulsion that allows the reaction to continue at a near-constant rate until it approaches completion. The approach by Deffense (2002) differs in that it aims to create a very large interface by using a high-shear mixer so that the reaction becomes so fast that it is complete before the emulsion has had time to coalesce and thereby lower the rate. The reason I discuss this mechanism in some detail is that similar arguments will be used when discussing enzymatic degumming processes.

Both degumming processes using EDTA can lead to very low residual phosphorus contents because it has a larger affinity for divalent metal ions than PA. In addition, they can be incorporated into a detergent dewaxing process (Gibon and Tirtiaux 1999). However, both processes use EDTA, and, especially on a molar basis, this is an expensive reagent to use in appreciable amounts. It is for that reason that I considered (1998) these processes to be suitable only as a kind of after-treatment that

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[9] See also http://lipidlibrary.aocs.org/processing/chem-degum/index.htm, written by Deffense.

[10] Etienne Deffense was research manager of Fractionnement Tirtiaux S.A. and is a co-inventor of the SOFT degumming process (Jamil et al. 2000). In 1995 he started his own company (Crystallisation & Degumming s.p.r.l.) to which he assigned the patent rights of his own invention (Deffense 2002). However, he did not pursue his European application, which therefore lapsed.

consumes very little EDTA, for instance, as a means of removing iron from palm oil after deep-sea transport.

Ethanolamines are used to remove phosphoglycolipids from rice bran oil (Kaimal et al. 2004).[11] To this end, the crude rice bran oil is first degummed with water, and then the water degummed oil is treated with monoethylamine, diethylamine, or triethylamine. Depending on their amounts, the ethylamines also neutralize some of the FFA present in the crude rice bran oil. The mechanism of NHP removal by ethanolamines is not clear, but Zufarov et al. (2009b) suggest that the salts formed by the reaction of an FFA with an ethanolamine "may play an important role in converting the non-hydratable oil-soluble complexes with the divalent metals ions Ca and Mg into more hydratable species." They filed a patent application in the Slovak Republic that was published in 2009 (Zufarov et al. 2009a), but the EPO does not provide an abstract.

With respect to the acid degumming process, little development after 1990 can be reported. This is not surprising since in 1998 I characterized the process as obsolete. Just before 1990, the Cambrian Engineering patent (Kaji 1988) was published. It belongs to a family of three applications: Europe, Denmark, and Japan, each of which quotes a US priority, but no patent was granted in the US. Like the Unilever Superdegumming process (Ringers and Segers 1977), it uses citric acid to decompose the NHP, but it differs in that the reaction temperature during this decomposition is maintained below 40°C. Not surprisingly, Unilever opposed and won, and the patent was revoked.

In 1991, Martens obtained a US patent in which he describes NHP as salts between two phosphatides and a calcium or magnesium cation. He realizes that decomposing these NHP with phosphoric acid leads to the formation of calcium phosphate that "is deposited on the drums of the centrifuges, which are used to separate the soapstock from the oil." He refers to a number of patents from 1941 to 1964 and also to the Segers process (Superdegumming), which has the advantage "that one can reach such a low phospholipids content that the thermal capacity of the oil is so great that the treatment may be completed with the physical refining, whereby the free fatty acids, color components, and aromatic components may be separated from the oil under vacuum with a thin film of steam stripping."

The invention for which the patent (Martens 1991) was granted is equally incomprehensible. I have spent quite some time on it, and I am afraid that this is the only conclusion I can come to. The main claim talks about an immobilized solid Lewis acid catalyst, which, according to the summary of the invention, can be aluminum oxide but is not further described in the detailed description of the invention. In fact, the only reason I mention this granted patent is to highlight that, apparently, nonsense can be protected by a patent provided it looks all right and there is no obvious

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[11] The front page of this patent ascribes it to "Thengumpillil et al." However, the full name of the first inventor is Narayana Balagopala Thengumpillil Kaimal, so it should have been ascribed to "Kaimal et al." N.B.T. Kaimal is a well-known Indian scientist who told me he has now retired when I asked him to clarify his and other people's names.

prior art. Sad but apparently true. I also Googled the assignee of the patent (Schelde-Delta bvba), but the only hit referred to this patent.

It is my impression that Unilever realized that its Superdegumming process needed a further degumming treatment for the oil to be physically refined, and so at one stage, hydratable phosphatides were added to oil (Segers 1979). Their role was to improve the stability of the dispersion of the degumming acid in the oil and so to facilitate the NHP decomposition. Another way to improve the Superdegumming process that has already been discussed in the previous section was the so-called Unidegumming process (Van de Sande et al. 1994, 1996),[12] which is in fact an acid refining process since the "agent promoting the formation of undissolved particles" is caustic soda. This lye raises the pH and causes PA to dissociate and move into the aqueous phase.

Yet another way to improve upon the Superdegumming process is disclosed in Segers (1997). Segers attempted to reduce the amounts of NHP in the crude oil by inactivating the enzymes that are considered to be responsible for NHP formation. Accordingly, the process entails that oilseeds or cake that result from cold pressing are conditioned in such a way that the period of time that its temperature lies between 30 and 80°C is minimized. The examples illustrate that very low phosphorus levels result when oil obtained from seeds that have been treated by the invention is acid degummed. In addition, residual iron levels are always below 0.01 ppm. It is interesting to note that dependent claim 8, which specifies the degumming step, includes the optional neutralization of the degumming acid by alkali, which is an acid refining feature.

The next patent I want to discuss (Silkeberg and Kochhar 2000) reminds me a bit of the Schelde–Delta patent (Martens 1991) in that my attempt to find out more about the assignee (Lipidia Holding S.A. in Luxemburg) only yielded hits concerning this patent. It aims to prevent the loss of antioxidants that are present in the crude oil during refining. On the title page, almost a whole columns of literature references deal with antioxidants such as sesamol etc. The patent is based on four separate provisional applications that led to an application that was filed only a few months later but abandoned and continued in part.

In many ways, it is a very narrow patent. It limits the oils to be treated to a few speciality vegetable oils such as sesame seed oil, tea seed oil, oat germ oil, and the like, and specifies a bleaching time in the main claim of about 15 to about 30 min. This means that bleaching a bit longer circumvents the patent. The "dedicated" bleaching process employs silica hydrogel and citric acid rather than bleaching earth. This causes antioxidant precursors such as sesamolin not to be converted to the antioxidant sesamol; that happens later when the oil is exposed to acetic acid as in mayonnaise. Deodorization also differs from standard practice in that it is carried out at a temperature of 120–150°C and employs nitrogen as stripping medium. Strangely enough, these conditions are not listed in the process claims.

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[12] These two patents go back to the same priority document.

Just as the above process was given a special name ("dedicated" refining), the patents to be discussed now also refer to a process given a special name: "organic refining."[13] It all started on 28 November 1998 with US application 09/197,953 that was published as WO 00/31219 on 2 June 2000, a hefty document numbering 69 pages, including the Search Report, and listing 41 claims.[14] During the coming years, this application led to six US patents (6,172,247; 6,172,248; 6,423,857; 6,426,423; 6,441,209; 6,844,458) and altogether 40 hits in the INPADOC patent family, related to 12 different countries. This represents a sizable investment!

So what does (Copeland and Belcher 2000) amount to apart from said investment? The so-called organic refining process is an acid degumming process using an organic acid "selected from the group of phosphoric acid,[15] acetic acid, citric acid, tartaric acid, succinic acid and mixtures thereof." As reported in the literature (Table 5 in Dijkstra and Van Opstal 1989), the use of acetic acid as a degumming acid should be avoided since iron chloride is oil-soluble.[16] Using acetic acid led to 2.00 ppm residual iron as opposed to 0.10 ppm for phosphoric acid and 0.07–0.19 ppm for the other "organic" acids.

Whereas the Superdegumming process (Ringers and Segers 1977) uses a concentrated solution of citric acid to decompose the NHP and then dilutes this concentrated solution to raise its pH and thereby encourage the PA to move to the aqueous phase, the "organic refining" process employs a diluted degumming acid solution. Referring again to the literature (Table 4 in Dijkstra and Van Opstal 1989), it is clear that acid strength matters. A phosphoric acid solution of less than 15 wt% leads to unacceptably high residual iron contents, and given the correlation between oil stability and residual iron content (Cleenewerck and Dijkstra 1992), it is highly doubtful if the citric acid strength of less than about 5% by weight (claim 5 in Copeland and Belcher 2000) will be sufficiently effective in iron removal. Poor degumming at low acid strengths has also been confirmed by Pan et al. (2001). In my opinion, the so-called organic refining process may work well with high-quality oils that contain hardly any NHP. On the other hand, oils that for whatever reason are difficult to degum will certainly not be degummed by this "organic refining process."

Given the size of the company, it is not surprising that Cargill also applied for patents in this field. One of these patents (Muralidhara et al. 2002) is remarkable in that it does not provide an example. It discloses a process to remove gums and

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[13] A glossary provided by Crown Iron Works (www.crowniron.com/glossary/index.cfm) defines the organic refining process as follows: "Acid Degumming enhanced by using large amounts of citric acid solution. As a result, residual amount of phosphatides in oil is very low, making process suitable for Physical Refining. Other main benefit is that heavy phase from separator can be decanted into free oil, gums and acid solution. The oil is recovered, the acid solution recycled and the gums sent to further processing. Process was developed by AG Processing and patented by IPH, USA."

[14] This may sound like a lot, but wait until we reach the patents dealing with enzymes.

[15] I consider phosphoric acid to be an inorganic acid.

[16] The Staley degumming process (Hayes and Wolff 1957) used acetic acid anhydride and was not pursued because of poor and unpredictable oil stability.

chlorophyll-related compounds from crude oil, especially from crude oil that has been produced by extracting frost-damaged oilseeds. According to the main claim, the crude oil must contain more than 1 wt% of gums, which corresponds to some 400 ppm P, which the process reduces to less than 50 ppm P. The process according to the main claim comprises three steps: first mixing the oil with acids (an aqueous mixture of sulfuric and phosphoric acid); then removing the gums that have been formed; and, finally, washing the oil with water. In addition, the main claim specifically excludes the use of alkali.

Even so, the main claim states that the water wash removes free fatty acids from the oil. I think this is highly unlikely since the aqueous phase was acidified at the outset and diluting it with water will not raise the pH sufficiently to convert the fatty acids into soaps and drive them into the aqueous phase. How then can the apparent FFA removal be explained? In order to answer this question, we should realize that the FFA content is determined by titrating a solution of the oil in a mixture of equal volumes of 96% ethanol and freshly neutralized diethyl ether with 0.1 N aqueous sodium hydroxide while using phenolphthalein as indicator. The volume used is then used to calculate the acid value of the oil or its free fatty acid content, which can, for example, be expressed as wt% oleic acid.

However, if the oil contains other acid compounds besides the FFA, these compounds also react with lye during the titration and thereby contribute to the acid value of the oil. The phosphate group in phosphatidic acid can act as such an acid compound, which is why the acid value of an oil decreases on water degumming. This decrease is not caused by FFA removal but by the removal of phosphatides. Accordingly, this could explain the unlikely statement in the main claim of Muralidhara et al. (2002) that washing an acid-treated oil with water causes free fatty acids to be removed from this oil.

The same explanation can be used to make sense of a patent application (Myong et al. 2007)[17] that has also been filed by Cargill. Like previous patents (Dijkstra and Van Opstal 1987; Mag and Reid 1980), the Cargill application stresses the importance of high-shear mixing during degumming by including this into the main claim. Other features included are a holding tank for the W/O dispersion and a separation step, and all this "such that the oil stream has a phosphorous (*sic*) content of not more than 20 ppm, and a free fatty acid content which is less than the free fatty acid content of the feed stream." The application publication Myong et al. (2007) also contains a figure with a mass balance (sheet 12 of 12). This shows that a crude oil containing 3.0 wt% phosphatides and 0.4 wt% FFA is acid degummed with 3 wt% of a 21 wt% aqueous citric acid solution to yield a degummed oil with only

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[17] I found reading this application most annoying. It contains many typing errors that are not detected by a spell checker, such as "steam" instead of "stream," and displays sloppy thinking: "Acid may be added to chelate non-hydratable phosphatides."

It also suffers from copy/paste anomalies. Comparison FIG. B is described as "a schematic drawing illustrating one example of a continuous enzymatic degumming process." There are no enzymes involved whatsoever. Even so, when FIG. B is discussed in paragraph [0056], this discussion includes an enzyme recovery and recycle operation.

0.175 wt% FFA. In other words, more than half the FFA went with the gum stream. Would you believe it! In fact, it ties in very well with the remark that (page 176 in Erickson 1995) "The FFA of good-quality soybean oil will be in the range of 0.5–1.0%, which will be reduced by 20–40% in the degummed oil." So on the face of it, there is prior art for this application.

Given its high-phosphatide and low-FFA content, the crude oil mentioned above is most likely to be soybean oil. The PE and PI present in this crude oil act as monovalent acids and therefore contribute to the acid value of the oil. Given the composition of the phosphatides in soybean oil, it can be estimated that a phosphorus content of 0.1% by weight corresponds to 0.43% FFA by weight.[18] Since the crude oil contains 3.0 wt% phosphatides, which amounts to 0.12% P, this corresponds to 0.52% FFA. Accordingly, the FFA content of the gums at 0.225% by weight on oil is even lower than the amount of 0.52% calculated on the basis of the phosphatides that are removed from the oil on water degumming.

The two Cargill patents above (Muralidhara et al. 2002; Myong et al. 2007) could raise an interesting legal question. Say you carry out the actions as specified in one or more of the claims and Cargill sues you for infringement. Will your argument that you do not remove free fatty acids but only lower the acid value of the oil get you off the hook? I think it should because the specifications only talk about free fatty acids. Had they mentioned somewhere that what they call free fatty acid content is just a notion that is calculated from the acid value of the oil, the situation might be different.

Carolina Soy Products is part of Whole Harvest Foods and prides itself on not using any organic solvents. Consequently, a degumming process patent assigned to this company (Dawson 2005) limits itself to soybean oil obtained by mechanical expelling; this greatly reduces the risk of prior art turning up unexpectedly and more or less ensures novelty. However, to merit a patent, the process must not only be novel: It should also be non-obvious, and this is where I find the process lacking. The claimed process comprises

(a) Mixing the expeller soybean oil with water or a weak acid
(b) Separating the gums from the degummed oil
(c) Mixing the degummed oil with lye
(d) Separating the soapstock from the neutral oil[19]

So far, this process does not differ from standard processing, but to make it look different, a limitation was included in this claim stipulating that the amount of calcium and magnesium remaining in the oil is less than 100 ppm. We know that these alkaline earth metals are removed on alkali refining (Hvolby 1971), so this limitation

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[18] I want to express my gratitude to J.C. Segers for providing me with this relationship.

[19] Column 3 of the patent lists a number of process steps that also include the production of the crude soybean oil. Step f) refers to the neutralization step and states that "the weakly basic aqueous solution reacts with the calcium and magnesium ions to produce soapstock." I thought that soapstock resulted from the reaction between the base and free fatty acids.

is as meaningless as stipulating that the oil density must be less than 1,000 kg/m^3; it always is. Accordingly, I think that no patent should have been granted, and in Europe, an opposition would in all likelihood have led to the patent being revoked.

With respect to the acid refining process in which the NHP are decomposed by a finely dispersed degumming acid that is then partially neutralized with caustic so that the liberated PA dissociates and becomes hydratable, the first patent I want to discuss is a Unilever patent (Van den Broek et al. 1991).[20] I regard this patent as a countermove against the Vandemoortele TOP degumming process. It claims a straightforward acid refining process, but in line with the Superdegumming process (Ringers and Segers 1977), it specifies that the gums be conditioned at a temperature ≤70°C or (claim 2) ≤40°C. Because at these low temperatures things do not happen that quickly, it introduces a further distinction from TOP by specifying a longer holding time during gum conditioning.

The second patent meriting discussion is the Krupp patent (Rohdenburg et al. 1993), which is based on work done in Hungary. Like the Unilever patent (Van den Broek et al. 1991), it discloses a low-temperature acid refining process. Accordingly, it also claims dewaxing, which ties in with the Martfü plant processing mainly sunflower seed.[21] Using more base than necessary to neutralize the degumming acid leads to soap formation, and this facilitates the removal of the wax crystals via a kind of detergent winterization approach.

The specification stresses that contrary to the prior art, which prescribes a high degumming temperature and a rather concentrated degumming acid (Alexander 1980) and violent dispersion of the acid (Dijkstra and Van Opstal 1987), the process according to the invention can completely avoid such extreme conditions. I have no doubt that some of these remarks have been made for "patenting reasons," to stress the inferiority of the prior art, to highlight the differences between the process of the invention and the prior art, and to introduce the surprise element. After all, the reaction between the aqueous degumming acid and the NHP in the oil phase needs contact to proceed.

The priority date of Rohdenburg et al. (1993) is 23.08.90, which is slightly later than the priority date (04.05.90) of Van den Broek et al. (1991). Consequently, Unilever could have opposed the Krupp patent after it had been granted at the end of 1994. No opposition was filed, and Unilever allowed its own patent to lapse after it had been granted.

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[20] Granting took a long time. The priority date is 04.05.90, and the patent was only granted on 06.08.97. No opposition was filed.

[21] In 1992, the AOCS organized a World Conference in Budapest that I attended. I visited the Martfü plant but was not allowed to see the degumming section. This was also the first time I met Dr. Katalin Kővári, who presented a poster on this degumming process. She knew what she was talking about, and the patent specification also reflects sound insight.

5.3 Membrane degumming Processes

In 1976, Sen Gupta developed a chromatographic method of separating phosphatides that was based on their tendency to form micelles when dissolved in an organic solvent. He also used this phenomenon as the basis for a degumming process for triglyceride oils (Sen Gupta 1977). Because of this micelle formation, the phosphatides can be retained by a semi-permeable membrane that allows solvent and triglycerides to pass. The organic solvents used in this process are inert hydrocarbons such as hexane, halogenated inert hydrocarbons, esters such as the ester of a lower fatty acid with a lower monohydric alcohol, and carbonyl compounds such as acetone. Most of the examples use hexane, but ethyl acetate and chloroform are also used.

Sen Gupta mentions several membrane materials such as polyacrylonitrile, polysulphone, and polyamide. He claims that they should be anisotropic and oil-resistant, have a certain cut-off limit, and have a minimum mechanical strength to withstand the pressure that has to be applied during the filtration to overcome the osmotic pressure. His last claim specifies the use of miscella obtained during solvent extraction of oilseeds.

By mixing a polar solvent like a lower alcohol or a ketone with the apolar hexane, some phosphatides are made to aggregate into micelles, whereas others remain in solution. Consequently, a fractionation of phosphatides becomes possible (Sen Gupta 1985b), whereby phosphatidylcholine can be recovered from the permeate.

In a subsequent patent (1985a), Sen Gupta discloses an improvement that involves the use of an additive selected from the group consisting of shea gum, surfactant, soap or their mixtures, or a basic additive that can form a soap with the free fatty acids present. He claims the same membrane polymers as before but also includes polyimides. He could do this since his priority dates from 21.04.82, which is earlier than the European publication dates (16.11.83) of Tanahashi et al. (1988) and (07.12.083) of Iwama et al. (1983), applications that also claim polyimide for the membrane. In 1990, a process was disclosed by Miki et al. involving a miscella concentration using a polyimide membrane in a first step and a separation between triglyceride oil and phosphatides in a second step using a polyethersulfone membrane. The application (Miki et al. 1990) has not resulted in a patent, and no applications have been filed outside Japan.

In the early 1990s, two patents were assigned to Rochem Separation Systems (LaMonica 1994, 1996), which are the only patents that this company, with its head office in Mumbai, India, ever acquired in the US. The first of these patents claims a refining process in which a miscella is subjected to membrane filtration and the permeate consists of refined oil that is free of impurities and organic solvent. In other words, the membrane also retains the solvent. This is most surprising indeed since solvent molecules are much smaller than triglycerides. This unlikely characteristic is also repeated in the second patent, which leads me to characterize these granted patents as a waste of money.

In 1992, Suzuki et al. disclosed a miscella filtration process using ceramic membranes with a filter pore size of 30–100 Å. To increase the flux, they lowered the miscella viscosity by raising its temperature to 50–90°C. In their example, they start with a soybean oil miscella containing 1–2% by weight of phosphatides and on membrane filtration, this is reduced to 20–30 ppm P in the permeate. Sadly enough, the example does not report the residual oil content of the retentate. The specification does not suggest diluting the retentate with further hexane and subjecting this diluted miscella to a further membrane filtration. Given the uncertainty of arriving at phosphatides with a low oil content and the high cost of ceramic membranes, it is not surprising that the process has not been used industrially.

Then, in 1999, Cargill filed a patent application that led to a PCT publication (Jirjis et al. 2000) and a whole string of 26 further applications, continuations in part, and granted patents such as, but not limited to, Jirjis et al. (2001, 2004, 2005, 2009). Some of them focus on how to condition the membrane used to degum a miscella, others more on its use or products. The membranes mentioned are made of the same polymers as claimed earlier: polyacrylonitrile, polysulfone, polyamide, and polyimide.

Soon after, Kőseoğlu, who at Texas A& M University had already worked on the use of membranes for various applications (Kőseoğlu et al. 1990; Kőseoğlu 1991), also applied for a degumming patent on 24.05.00 that was later granted as it specifies the use of an ultrafiltration membrane made from a polymer or copolymer of a vinylidene difluoride monomer[22] (see also Wang et al. 1999). The use of this monomer in membranes used to degum oil was subsequently described in the literature that was published after the priority date in Ochoa et al. (2001) and Pagliero et al. (2001). However, the second of these articles refers to the *Proceedings of Euromembrane99*, a conference held in 1999 in Louvain, Belgium, which precedes the priority date. If the use of vinylidene difluoride was made public at this conference, it could well constitute prior art for Kőseoğlu et al. (2004).

This context provides me with an opportunity to explain an aspect in which US patent law differs from, for instance, European practice. In Europe, anything published before an application date is considered to be prior art that destroys novelty. The US, on the other hand, makes an exception for publications naming one or more of the applicants as author and dating less than a year before the priority date. So if the person who presented the paper in Louvain had applied for a US patent within a year after his presentation, his presentation would not have been held against him and would not have been regarded as prior art. For US inventors, this difference can be very treacherous. They present a paper in good faith that their year's grace does not prevent them from obtaining a patent. That holds for the US, but in Europe, they can forget about it.

Coming back to the miscella degumming patents granted to Cargill and Texas A&M, semitechnical or even industrial trials have been carried out and they were found to suffer from serious membrane fouling.[23] Therefore, membrane degumming is not (yet?) used industrially, and the likelihood that Cargill lost interest in its membrane degumming process is illustrated by a paper by Cargill authors

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[22] This chemical name is a pleonasm. The vinylidene group has two free bonds just like the methylene group (–CH_2-). So methylene chloride is CH_2Cl_2 and vinylidene fluoride is CF_2=CH_2 or 1,1-difluroethene.

[23] I acknowledge the personal communication from S.S. Kőseoğlu 2011, who also pointed out the existence of US patent 6,140,519, which I will discuss ahead.

(Gupta and Muralidhara 2002) in which they describe a separation process of the retentate that is not a subject of a patent application. Moreover, the article does not refer to the Cargill membrane degumming patents either.

Apparently, the Unilever patent (Den Bieman et al. 2002) that specifies back blowing with gas, back flushing with oil, and washing with alkali when the flux through the membrane starts to diminish did not provide a sufficiently effective remedy. Perhaps ceramic membranes (Inui et al. 2001; Subrahmanyam et al. 2006; Wang et al. 2004) can withstand more vigorous cleaning, but for industrial application, they are still too expensive.

Ceramic membranes are also used in the process disclosed in (Jeromin et al. 1994) not to filter the oil but rather to recuperate water from washing water. Crude oil is washed with acidified water, which causes impurities to move into the aqueous phase. This phase is then concentrated by ultrafiltration and the clean permeate is recycled.

In fact, the only membrane application in edible oil processing that is used industrially has been disclosed by Hutton and Guymon (2000). It concerns a deoiling process for lecithin using polyvinylidine (*sic*) fluoride membranes. In this process, lecithin is dissolved in an alkane like hexane and the resulting solution is passed along a membrane; as a result, hexane and the oil that was present in the lecithin pass through the membrane and the phospholipid micelles are retained. In lecithin, the ratio of oil to phosphatides is 0.7 (w/w), whereas in crude oil with a phosphorus content of 800 ppm P, this ratio is about 50. So Hutton and Guymon remove far less oil than when crude oil is degummed, and maybe this is why their process is operated on an industrial scale.

The deoiled miscella can then be bleached and the deoiled lecithin is recovered by evaporating the hexane, for instance, by using a chrome-plated or stainless steel desolventizing drum; finally, the deoiled lecithin can be granulated.

According to a German application (Saft and Heilmann 2002), miscella is first concentrated by the evaporation of hexane to a residual hexane content of 0.3–10% and then the concentrate is just degummed with water. In the example, this water degumming reduced the phosphatide content of the oil from 2.0 to 0.08%, which corresponds to some 27 ppm phosphorus. This is low and looks promising. Moreover, the hexane lowered the oil viscosity, and this reduced the oil entrainment by the gums, which is also an advantage. However, I am not aware of any publicity for this water degumming process, so on closer investigation, it may have turned out to be too good to be true.

5.4 Enzymatic Degumming Processes[24]

In 1990, enzymatic degumming was not yet practiced industrially. In fact, the only patent in my literature database under the heading "Degumming, enzymatic" that dates prior to 1990 is an application (Tirtiaux et al. 1983) that never made it to a

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[24] See also http://lipidlibrary.aocs.org/processing/degum-enz/index.htm.

granted patent. A request for examination was made at one stage, but when the applicants did not reply to an Office Action within the statutory period, the application was deemed to be withdrawn; if any applications were ever filed outside Europe, they never resulted in a granted patent or application publication. The main claim of this application is quite wide in that it specifies the treatment of an oil or fat that may be animal or vegetable, crude, treated, or fully refined, with at least one enzyme catalyzing the hydrolysis or depolymerization of non-glyceridic components of said oil. Claim 3 specifies enzymes selected from the group consisting of phosphatases, pectinases, and so forth, and the text specifically mentions phospholipase C.

This raises the semantic but intriguing question of whether or not phosphatides are to be regarded as non-glyceridic compounds. There is no doubt that phosphatides contain a glycerol moiety, and so it can be argued that they should be regarded as glyceridic rather than non-glyceridic compounds. On the other hand, the patent application states quite clearly (page 1, lines 10–13) that phosphatides are henceforth to be covered by the term "non-glyceridic." So there can be no doubt that Tirtiaux et al. (1983) disclose treating oils with phospholipase C or D since these catalyze the hydrolysis of bonds to the phosphate group in the phospholipids.

Two other early documents (Graille et al. 1988a, 1988b) refer to the potential advantage of using phospholipase C (PLC). They explain that the use of PLC would convert phosphatides into oil-soluble partial glycerides and water-soluble phosphate esters and thereby cause the oil yield to increase. They mention the PLC from *Bacillus cereus* but also point out that it was much too expensive to be economically viable.

Then, in 1992, the AOCS organized a World Conference on Oilseed Technology and Utilization in Budapest, Hungary. Lurgi contacted the AOCS saying that it wanted to present a paper at this conference to launch EnzyMax®, its enzymatic degumming process. The AOCS pointed out that this conference had invited speakers only, but to accommodate Lurgi, it was suggested that I include the EnzyMax® process into my presentation on oil refining (Dijkstra 1993). To prepare my presentation, I visited Lurgi in Frankfurt am Main but learned very little. However, I received some oil samples that I was told had been obtained by enzymatic degumming. We analyzed them at Vandemoortele so that I could at least report that residual "phosphorus levels were close to 4 ppm irrespective of starting levels and residual iron levels were as low as 50 ppb." Having been told hardly anything about the process, I could not be specific, raise questions, or be critical either.

After my presentation, Lurgi organized its own launch for an invited audience in a nearby hotel and there I learned a bit more about the process (Aalrust et al. 1993). Enzymatic degumming also became the subject of literature articles (Buchold 1993; Dahlke et al. 1995) and a patent granted to Showa Sangyo Co. Ltd. (Yagi et al. 1996). This company also applied in Europe (Yagi et al. 1994) and a patent was granted. It was opposed by Lurgi and AB Enzymes GmbH (the new owner of Röhm GmbH, an enzyme producer that jointly owned the EnzyMax® patent with Metallgesellschaft AG). The opposition was successful and the patent was revoked. Showa Sangyo appealed against this decision, but finally, in 2004, this appeal was rejected.

The patent itself (Yagi et al. 1996) discloses an enzymatic degumming process employing so much water that the oil to be degummed is dispersed in the water phase containing the enzyme. The degummed oil has to be washed, and this step also uses a relatively large amount of water that can be acidified to a pH of 3 to 6. Oil thus treated can be bleached and then neutralized by a vacuum stripping process.

Learning more about enzymatic degumming enabled me to become more critical, so when I presented a paper on degumming at the AOCS Annual Meeting & Expo in Chicago in 1998, I commented as follows:

- It raises more questions than it answers
  - buffer below optimal pH of phospholipase A_2
  - calcium co-factor not available because of citrate buffer
  - no gum analyses published
  - lyso-phosphatides are hardly more hydratable
- The enzyme is not kosher
- Could well be acid refining process “in disguise”

And indeed, working on this chapter convinced me that industrial enzymatic degumming processes using a phospholipase A depend on a prior acid degumming treatment to arrive at a low residual phosphorus content (Dijkstra 2010b). The phospholipase-catalyzed hydrolysis is just too slow to act on the NHP.

This characteristic was well known to the enzyme producer himself, who states (Löffler et al. 1999)

> In the “EnzyMax process,” the advantageous effect of the citric acid can be utilized for extensive degumming, specially by citric acid treatment which precedes or follows the enzyme treatment. Simultaneous use of citric acid and enzyme is not possible.

Another Röhm patent (Buchold et al. 1996) discloses an improvement to the enzymatic degumming process in which the gums are treated with a “separation promoter” that permits a “substantially sludge-free solution that contains the enzyme” to be recovered and recycled. Without this separation promoter, recycling the enzyme implied that gums were also recycled, necessitating a purge that also caused enzyme to be lost.

Because the PLA_2 used in the EnzyMax® process was not kosher, quite expensive at $143.75/kg (Dahlke et al. 1995), and a byproduct of insulin production, it soon became clear that in the long term, a microbial enzyme would be welcomed. Accordingly, Röhm AG isolated an enzyme from *Aspergillus* that has PLA_1 or PLA_2 activity, or both, and claimed a degumming process (Löffler et al. 1999) using these enzymes. In a subsequent, protein engineering–oriented patent (Löffler et al. 2000), a cleavage fragment having phospholipase activity was claimed. This patent belongs to a family of 14 applications, which indicates that at that time, Röhm AG considered enzymatic degumming to be quite important.

Another enzyme manufacturer, Novo Nordisk A/S, also developed an enzyme (Lecitase® Novo) that was obtained from *Fusarium oxysporum* (Clausen et al. 1998b; Clausen 2001). A patent was applied for (Clausen 1999), a request for examination was filed, and renewal fees were paid up until patent year 5, but no further fees were paid and the application is therefore deemed to be withdrawn. Lecitase® Novo is a phospholipase A_1 (PLA_1) that is so active that it can be used to degum crude oils as well as water degummed oils. Its optimal temperature range is 40–45°C and since the centrifugal separation requires a higher temperature to reduce the viscosity of the oil, the temperature increase will inactivate the enzyme so that it cannot be recycled.[25]

The enzyme Lecitase® Novo can also be used in a kind of enzyme-assisted, dry degumming process (Nielsen and Clausen 2002). In this process, the water degummed oil is first treated at a temperature of, for instance, 70°C with citric acid to decompose the NHP. Then the oil is cooled to 40–45°C, the acid is partially neutralized, and the enzyme is added and allowed to react for at least 2 h. Bleaching earth and/or silica hydrogel are added and finally removed by filtration. The presentation by Nielsen and Clausen (2002) does not mention if the temperature is raised to increase the rate of filtration and reduce oil retention in the filter cake. The process does not require a centrifuge and does not lead to any aqueous effluent.

Work at Novo Nordisk continued and led to the development of an acidic phospholipase that catalyzes the hydrolysis of both fatty acid groups in phosphatides (Hasida et al. 2000). Example 6 shows the enzyme to be active between pH values of 3.5 and 5 and in a temperature range of 35–40°C. For existing installations, these temperatures are quite low, and perhaps that is the reason why as far as I know, this enzyme has not been commercialized for enzymatic degumming.

Instead, a different approach was adopted that led to a novel enzyme (Lecitase® Ultra) by taking the coding for the phospholipase activity from *Fusarium oxysporum* and adding it to the lipase from *Thermomyces lanuginosa*, replacing the lipase production coding. This yielded a hybrid with the better thermal and pH stability of the *Thermomyces* and the phospholipase of the *Fusarium.*[26] This work led to a patent application (Clausen et al. 1998a) containing 70 claims. The patent as granted still contained 70 claims, but it was opposed by Danisco A/S, Denmark, and DSM, the Netherlands,[27] and finally, the patent was maintained in an amended form that lists only three claims. These are very much concerned with polypeptides with specified amino acid sequences. The two US family members (Clausen et al. 2000a, 2000b) also lost most of their original claims before being granted.

Another enzyme used in industrial enzymatic degumming processes is phospholipase C. This enzyme is the subject of a provisional US application (60/374,313)

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[25] The manufacturer presents this as an advantage because it saves the refiner a lot of bother. I would rather describe it as an advantage to the enzyme manufacturer who will sell more enzyme.

[26] I acknowledge the receipt of this explanatory background information from W.D. Cowan.

[27] This company produces its own phospholipase A_2 (GumZyme®), as disclosed in (Albermann et al. 2007, 2010).

that was filed on 19 April 2002 and led to an ever-increasing number of published documents[28] that even include a few granted patents. This provisional application led to application 10/421,654, filed on 21 April 2003, that was published as US 2004/0005604 and subsequently abandoned to be continued in part as application 10/796,907, filed on 8 March 2004,which led to Application Publication US 2005/0108789, which led to US Patent 7,226,771 (Gramatikova et al. 2007). Application 10/796,907 also led to a continuation in part that was filed on 8 March 2005 as a PTC application (PCT/US05/07908) that resulted in US Application Publication US 2008/0317731 (Gramatikova et al. 2008) and a divisional application that was filed on 29 July 2008 and published as Application Publication US 2009/0053191.

The earliest publications mention only four inventors, but those that took the PCT route mention 17 inventors, including the original four. The US publications mention Svetlana Gramatikova as the first inventor, but in other countries, other inventors may be mentioned first.[29] All these publications concentrate on protein engineering, and only a few of the claims pertain to edible oil degumming since other applications of the enzyme, such as the purification of a phytosterol or a triterpene, are also covered. Claims specifying the use of the enzyme are limited to the enzymes as specified in the patent document, which eliminates the risk of prior art turning up during examination and/or opposition.

Claim 251 (!) in Gramatikova et al. (2008) is concerned with a "process for reducing gum mass and increasing neutral oil gain through reduced oil entrainment" by using the Purifine® enzyme.When Barton introduced this enzyme in 2007 during the AOCS Annual Meeting & Expo held in Quebec City, he rightly stressed this aspect. Edible oil prices had recently shot up and yield had become very important indeed. In 2005 and earlier, when oil prices were still reasonable, this aspect was never stressed (Cowan et al. 2005), and this potential advantage of the enzymatic degumming process was not discussed when Lurgi launched its EnzyMax® process in 1992 either. However, in 2007, De Smet (Gibon et al. 2007) cottoned onto the yield increase, stating, "It has been demonstrated on an industrial scale that enzymatic degumming is a cost-effective process that can result in lower oil losses."

Accordingly, the PLC-catalyzed degumming process improves the oil yield via two different mechanisms: It converts PC and PE into diglycerides that remain in the oil throughout its further downstream treatment, and it reduces the neutral oil loss by entrainment with the gums by hydrolyzing part of the gums. According to Hitchman (2009), this can amount to 2.0% oil yield improvement, which has been demonstrated on a laboratory scale and confirmed by plant trials.

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[28] In a recent review (Dijkstra 2009), I advised readers to search for Inventor: gramatikova; Assignee: diversa. Doing that myself in Espacenet provided me with a rather short list, but when I then went to look at the family members, there were 27 hits, 8 of which referred to an application by Kurita Water Ind. Ltd. referring to permeable membranes. This shows that there is room for improvement, as if we didn't know that already.

[29] The Chinese application CN 101426981 even mentions CHARLES SAAC as the inventor; they mean Charles Isaac.

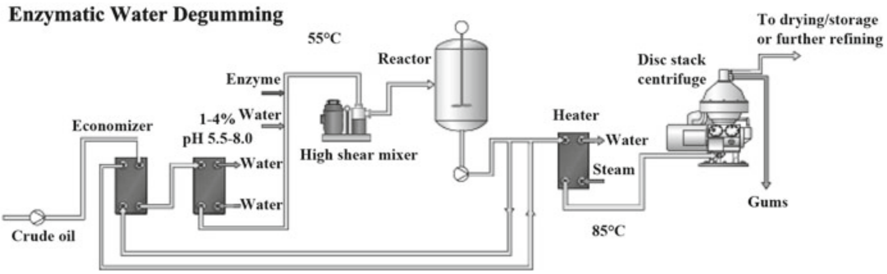

Fig. 5.3 Degumming process flow diagram (adapted from Hitchman 2009)

Accordingly, the PLC-catalyzed degumming process can improve the oil yield in comparison with the water degumming process, and the degummed oil may have a slightly lower residual phosphorus content than water degummed oil, which may still contain some PE. On the other hand, as indicated in Fig. 5.2, the degummed oil resulting from the enzymatic degumming process still contains NHP and therefore needs to be alkali-refined or to undergo an acid refining treatment before it can be physically refined. If the residual phosphorus content is not too high and/or the oil is rather dark, a dry degumming treatment followed by physical refining can also be considered.

To illustrate how to use the enzyme, a flow diagram is shown in Fig. 5.3, which was adapted from a slide that was presented by Hitchman in 2009. The degumming process in Fig. 5.3 is quite simple. Oil is heated to reaction temperature, and then water and enzyme are added, mixed into the oil, and allowed time to react. Then the oil is heated to reduce its viscosity and improve separation in the centrifugal separator. During this heating, the enzyme is inactivated, which means that residual PC and PE in the gums will not be hydrolyzed.

The enzymes discussed so far catalyze the hydrolysis of phosphatides. There is also an enzyme, lipid acyl transferase (LAT), that catalyzes a kind of ester interchange in which one ester bond is broken and another is formed. In this particular instance, the ester bond that is broken is the ester bond between a fatty acid and a glycerol moiety, and the bond that is formed is between that fatty acid and a sterol or stanol present in the oil. Such an enzyme has been disclosed by Sø and Turner (2007). The priority documents of this patent application (GB 04/16035.4 and GB 05/13859.9) are the same as those of a later application (Miasnikov et al. 2008). Both applications are continuations in part of PCT applications. Finally, a lipid acyltransferase has been claimed in Kreij et al. (2009)[30] under the title of "Protein."

Danisco A/S has also applied for a degumming process patent (Sø and Brown 2009); it is interesting to note that the main claim just mentions "a lipid acyltransferase" and is therefore not linked to any polypeptide with a specified sequence identity. At first sight, the validity of such a broad claim might look doubtful, but the

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[30] This application covers 390 pages, so I only printed the claims.

priority document of (Sø and Brown 2009) dates from 21 December 2007 and thus predates the publication date (27 December 2007) of (Sø and Turner 2007) by a few days. Consequently, this publication claiming "A process of enzymatic degumming edible oils …lipid acyltransferase" does not constitute prior art.

In addition to claiming a process to degum a preferably crude edible oil, the application by Sø and Brown (2009) also claims subsequent incubation of the gum phase containing the enzyme and separating the oil from the residual gums after up to 7 days. This kind of process will be discussed in more detail later on.

Transferring a fatty acid moiety from a phosphatide to a sterol present in the oil has the advantage that the resulting lysophosphatide is hydrophilic and that the fatty acid is not lost during subsequent refining operations. In this respect, the use of LAT offers a yield advantage over the use of PLA_1 and PLA_2. However, on a molar basis, the crude oil to be degummed using LAT may contain more phosphatides than sterols. In that instance, sterols can be added to the oil before it is treated. If no sterols are added, some of the fatty acids liberated from the phosphatides end up as FFA and will thus be lost during subsequent refining. Also, the rate of the reaction leading to FFA is about ten times slower than the rate of the fatty acid transfer reaction leading to esterified sterols.[31] Another difference is that the transfer only affects the β- or 2-position of the phosphatide, whereas the hydrolysis affects both positions.

Contrary to the Purifine® PLC discussed above, the LysoMax® LAT enzyme acts on all phosphatides it can reach. Being hydrophilic, it does not act on the NHP that are dissolved in the oil. This means that a low residual phosphorus content after LAT degumming can only be attained if the NHP are decomposed by a degumming acid before the enzyme is added to the oil. A preliminary acid refining treatment is therefore mandatory (Dijkstra 2010b).

Süd-Chemie has also entered the enzymatic degumming field by collaborating with Prof. Bornscheuer of the University of Greifswald. This has led to a first application (Jackisch et al. 2007) that is deemed to be withdrawn and a second one (Jackisch et al. 2008) referring to the same priority documents and that is still being examined. The application discloses a thermostable phospholipase C that is still active at 90°C. The last example describing a degumming experiment pre-treats the oil to be degummed with citric acid that is subsequently partially neutralized to provide a citrate buffer that keeps the pH between 5 and 6. After a reaction period of 6 h, the residual phosphorus content of the oil is less than 5 ppm. So it looks as if this enzyme also needs an acid refining pretreatment to be effective, but the sting is in the tail: "The same low phosphorus contents were obtained when a water degummed oil with a phosphorus content of about 45 ppm was directly subjected to the enzymatic degumming as set out above."

Another company not directly involved in oil degumming is DSM, which acquired Gist-Brocades, an important producer of yeast, penicillin, and enzymes—hence

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[31] I am most grateful to J.B. Sø (Danisco A/S) for answering a list of questions and providing me with valuable background information.

DSM's interest in phospholipase (Albermann et al. 2007)[32] to be used primarily in dough. In enzymatic degumming, enzyme immobilization has also been reported. A Japanese patent application (Kosugi and Rakushitto 1999) was published disclosing the immobilization of PLA_1 and/or PLA_2 on a cation exchanger, but according to the Espacenet database, this application has not led to granted patents either in Japan or elsewhere. This database also revealed the existence of a Chinese patent application (Yu et al. 2007)[33] claiming all kind of advantages for phospholipase immobilization, and finally, a US application (Chou 2009) immobilizes all the phospholipases indicated in Fig. 5.1 and claims to degum crude oils containing non-hydratable phosphatides.

Given the doubts expressed above about the ability of phospholipase enzymes to cause NHP to be hydrolyzed in an industrial reactor, this application sounded like a most intriguing document indeed. It turns out that it originates from the biodiesel industry. So diluting the oil to be degummed with fatty acid methyl ester (FAME) to reduce its viscosity does not impede its downstream conversion to FAME. However, the main claim does not mention this dilution. It merely prescribes the following: treating the crude oil containing NHP with an immobilized phospholipase; mixing the treated oil with water or an aqueous solution; and separating the oil from the water. Sounds too good to be true.

So apart from mixing the oil with FAME, there is another trick required to make the process work. The water used to wash the treated oil must contain an acid such as citric acid, a chelating agent such as EDTA, or both, and it can also contain a surfactant. Accordingly, Chou (2009) proposes a SOFT degumming process that is preceded by an enzymatic degumming process to convert the hydratable phosphatides into breakdown products that retain less oil.

Before discussing the use of more than one enzyme or enzyme mixtures, I just want to refer to two further Chinese applications. The first one (Wan 2006) introduces ultrasonics into enzymatic degumming, but from the abstract it is not clear if this kind of treatment affects the hydrolysis of NHP. The second one (Wu 2009) is limited to the enzymatic degumming of camellia oil.

The first process, "wherein said enzyme of the reacting step is selected from the group consisting of any lipase A_1, A_2, B, C and D," aims at reducing the fouling of centrifugal separator discs (Dayton et al. 2007). It claims to achieve this laudable object by adding a food-grade acid to the degumming mixture after the enzyme has had time to catalyze the hydrolysis of the phosphatides present in the oil being degummed. The resulting low pH "prevents calcium citrates from forming and precipitating out." The Literature Search Report published with Dayton et al. (2005)

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[32] I became aware of this patent through the patent review in *Inform* **21**, (2) 102–104, an extremely valuable feature written by Scott Bloomer.

[33] The bibliographic data provided by Espacenet list the inventors as DIANYU YU;YUQING SONG; JUNGUO WANG, etc. From similar documents mentioning names, I know that they list the inventors' surnames first and then their given names. However, since Wang is the most common surname in China, I get the impression that the first inventor of this patent is a Mr. Yu and that is the reference used.

lists five category X documents; they may well complicate a patent being granted. To me, the most interesting feature of this application is the 38 examples.

The conclusions that the application draws from these examples concern the reaction time, the pH, simultaneous addition of the enzymes *versus* consecutive addition, temperature, and so on. My conclusions are different: Without acid refining, the residual phosphorus content is invariably high, and all low levels of residual phosphorus result from experiments that started with an acid refining step. I therefore summarized the salient data of the examples in a table (Dijkstra 2010b) that shows quite clearly that all experiments leading to a low residual phosphorus content comprised an acid refining step, and all experiments without an acid refining step led to high residual phosphorus levels.

Finally, phospholipase enzymes can also be used in the treatment of gums. As disclosed by Kellens and De Greyt (2006), gums obtained by treating a crude vegetable oil with water can be mixed with a phospholipidolytic[34] agent. This then causes the phosphatides to hydrolyze so that their ability to retain oil is reduced. Consequently, an oil phase is formed that can then be recuperated. One of the phospholipidolytic agents disclosed is a phospholipase, and Example 4 describes how phospholipase A_1 (Lecitase® Ultra) caused a phase separation in the gums treated with this enzyme.

Obtaining a patent for this oil recuperation process in the US turned out to be unexpectedly difficult because of a persistent lack of understanding on the part of the Examiner. This situation was resolved by submitting an affidavit or DECLARATION UNDER 37 CFR 1.132 that was drafted by the De Smet patent agent in the US and that I modified and signed as an expert in the field. This declaration started with a short *curriculum vitæ* and then I went on to declare

> [0006] Although I am officially retired, I continue to be active in the field of edible oils and fats as an author, editor, inventor, and consultant. In this latter capacity, I am presently a paid consultant working for the assignee of the present application.
>
> [0007] I am familiar with the above identified patent application, the Office Action dated March 19, 2009, and the reference patents relied upon by the Examiner in that Office Action." *Etc.*

It worked. US Patent 7,696,369 B2, Kellens et al., Oil recuperation process, was duly granted on 13 April 2010.

Another patent application (Dayton 2009) discloses that when gums are treated with an enzyme with PLA activity to generate free fatty acids and an enzyme with PLC activity to generate diglycerides, the result is that these two products combine to form triglycerides. Apparently, the phospholipase also has lipase (or esterase) activity and catalyzes the esterification of the partial glycerides. This is remarkable since this esterification takes place in an aqueous medium. Given the lipase activity of the enzyme, further hydrolysis of glycerides would therefore be more likely. The priority date of this application (07.01.2008) is later than the publication date of Kellens and De Greyt (2006) of 08.02.2006. Accordingly, the patent granted to

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[34] I was quite pleased with myself when I coined this word since it covers both acids and enzymes.

Desmet is prior art for the application by Bunge. Therefore, the A3 Search Report lists the Desmet patent but qualifies this with an "A" (document defining the general state of the art that is not considered to be of particular relevance).

This Bunge application (Dayton 2009) raises another interesting aspect in that the specification describes how the amount of free fatty acids and diglycerides that can be liberated should be calculated, but that description is fundamentally wrong. It prescribes somewhere that the phosphorus content (in ppm) of the oil should be multiplied by the relative atomic mass of phosphorus (30.97), which does not make sense; it should be divided by 31 to arrive at a molar equivalent. Question: Does this affect the validity of the patent? Not knowing the answer to this question but being greatly intrigued by it, I went to counsel.[35] So I learned that

> The validity of any patent that might result from the application depends on whether or not the mistake affects the claims. If correcting the mistake would still lead to the same conclusions being drawn from the examples or the general arguments put forward in the detailed description, patent rights will not be affected and the specification will just be an embarrassment to the people who wrote it. In the present instance where the application is a PCT application, a corrected application may be filed in the designated countries to avoid this embarrassment, but then, this deviation from the PCT application would have to be argued and justified. In the US, a continuation in part can be considered as a means to avoid this embarrassment, but that poses other problems. The best way is really to avoid this kind of mistake.

5.5 Dry and Miscellaneous Degumming Processes

With respect to the dry degumming process, little has been published since 1990. The oldest publication (Van Dalen and Van Putte 1992) is a journal article referring to a precipitated silica that was the subject of a patent application (Van Dalen et al. 1990). The publication describes a degumming experiment in which water degummed soybean oil with a phosphorus content of 173 ppm P was treated with citric acid at 90°C for a period of 15 min. Then a small amount of water was added and the mixture was again stirred vigorously for 15 min. The precipitated silica was added, and 90 min later, the mixture was dried under vacuum. This reduced the phosphorus content to 3.9 ppm P, which was further reduced to 1.4 ppm P after bleaching with an acid-activated bleaching earth.

The second patent published since 1990 (Shaw et al. 1993) is mainly concerned with bleaching earth characteristics such as its composition, mineral origin, particle size, etc. The patent can be regarded as Laporte's response to silica hydrogel developments by Crosfield and Grace. Just like some of the other clay producers, Laporte took the route of excessively acid-leaching clay to make a highly siliceous adsorbent. However, these adsorbents lack the performance of synthetic

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[35] Once again, I acknowledge the contribution by Scott Bloomer, who gave a rapid and comprehensive reply to my question.

amorphous silicas.[36] The Search Report of Shaw et al. (1993) lists a single category X document that only refers to a few claims. Even so, the application was not pursued. A possible reason for this lack of perseverance could be that around that time, Laporte Industries Ltd., the applicant, was leaving the bleaching earth business.[37]

The third patent (Schurz 2009) was granted to a company that is still quite active in bleaching earth, Süd-Chemie. It claims a low-temperature (35–55°C) dry degumming process that employs citric acid as degumming acid. It also prescribes a bleaching step that includes both a wet bleaching stage and a vacuum bleaching stage. At the time of this writing, this European patent had been granted only a few months earlier. In addition, a German and an Austrian equivalent were given as family members.[38] Since a large number of states were designated, the family may well grow. This European patent differs from the German Application Publication in that claim 1 in the granted patent incorporates claims 2 and 3 of the application; its scope has been restricted on examination.

Why would a company manufacturing bleaching earth seek protection for a bleaching process for edible oils it is not going to use itself since it does not operate any oil refineries? The answer is that when you sell a product for which you have obtained patent protection, you automatically allow your customer to use it. After all, you have already earned money from your patent by selling the product to this customer, so he cannot be expected to pay again in the form of royalties for a license. So Süd-Chemie can inform a potential customer about its advantageous bleaching process and persuade this customer to purchase its bleaching earth. Then the customer is allowed to use this marvelous process but only when using bleaching earth bought from Süd-Chemie. He would infringe on the Süd-Chemie patent if he used bleaching earth from another company. So by applying for a patent it is not going to use itself, Süd-Chemie nevertheless protects its own interests. That may well explain why a large number of countries have been designated in this European patent. The above arguments also explain why contractors apply for patents that protect processes they are not likely to use themselves.

Just as the acid degumming process has a counterpart in the dry degumming process, the acid refining process has a counterpart in what was first called a “modified acid refining” process (Nock 1993) and later “Sorbsil® acid refining” (Nock 1994a). Three patents claiming embodiments of this process have been applied for, and since Joseph Crosfield & Sons was at that time part of Unilever, it is not surprising that the main claims in the Crosfield applications (Nock 1994b, 1995) are almost identical to

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[36] I received this background information from A. Nock.

[37] In 2000, Laporte Industries sold its bleaching earth business along with other major business interests to Kohlberg Kravis Robert & Co. for $1.2 billion. At the time of this writing, Rockwood Additives Ltd., a subsidiary of Southern Clay Products Inc., produces the bleaching earth at the Widnes site. It is sold under the Fulmont name by AMC (UK) Ltd.

[38] This means that there is no equivalent in English.

the earlier Unilever application (Schmutzler 1993). The following table shows the slight differences between the three patents.

Patent reference	Schmutzler (1993)	Nock (1994b)	Nock (1995)
Step 1	Acidifying the oil with an acid		
Step 2	Partially neutralizing the acidified oil with		
	alkali	alkali	solid alkali
Step 3	Contacting the partially neutralized oil with		
	an amorphous silica	acid-activated clay	an adsorbent
Step 4	Removing solids from the glyceride oil		

Crosfield & Sons[39] produced sodium silicates, and so the Schmutzler patent really falls within their sphere of activities. I therefore have the impression that the Nock applications were filed to fill a gap that was inadvertently left by the Schmutzler patent. Neither patent was actively pursued, and I have not come across any literature that discusses the acid refining process in which the gums are removed by adsorption onto bleaching earth. The mechanism of the adsorption during dry degumming is one of the many unanswered questions that I listed in my Chevreul Award address (Dijkstra 2010c).

The miscellaneous degumming process I want to discuss is the process disclosed by Cavitation Technologies Inc. (Gordon et al. 2010). In Example 1 of this patent application, water degummed soybean oil with a phosphorus content of 137 ppm is mixed with 3% water and the mixture is passed through a flow-through cavitation device: “After cavitation, the concentration of phosphorus dropped to 8.82 ppm, which corresponds to a removal of 93.6% of the phosphatides.” I limit myself to just quoting what I read since I don’t know what to think of it. The process has been the subject of a recent oral presentation (Svenson 2011).

5.6 Discussion

Given the developments of the last 20 years as outlined above, I now want to discuss the implications and which process should be adopted when, but I realize that these questions have no universal answers. The answers depend on a large number of variables, such as, but most certainly not limited to, which patent is still in force in which country, local circumstances (markets, regulations, labor and energy costs, to name a few), and plant hardware that has already been installed.

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[39] The company Joseph Crosfield & Sons dated from 1814. It started as a soap-making business. In 1911 it was purchased by Brunner, Mond & Co., one of the companies that became part of ICI, and in 1919 it was absorbed into Lever Brothers, which merged into Unilever in 1929. In 1997, it was acquired by ICI and in 2001, Ineos Capital purchased the company. The name Crosfield was finally lost as it was renamed Ineos Silicas. Finally (?), Ineos Silicas merged with PQ Corporation and is now known under that name.

One answer is simple. If you want to produce lecithin, you have to degum crude oil with water and dry the gums. This water should not contain any acid since this will affect the phosphatide composition of the resulting lecithin. Until 1990, soybean lecithin was the only commercial product available, but since then, a niche market for sunflower oil lecithin has been created to prevent consumers from being exposed to products that originate from genetically modified material.

Another answer that is almost equally straightforward concerns oils with a low phosphatide content such as palm oil, the lauric oils, and animal fats. They can simply be subjected to the dry degumming process followed by physical refining. This is a well-proven and cheap option involving only two steps. However, with respect to the dry degumming process, several options have been reported in the literature:

- Degumming acid plus bleaching earth (Sullivan 1978);
- Degumming acid, water addition plus precipitated silica (Van Dalen and Van Putte 1992);
- Partial neutralization of degumming acid plus bleaching earth (Nock 1994b);
- Partial neutralization of degumming acid plus silica hydrogel (Schmutzler 1993).

Sadly enough, I am not aware of any literature reporting a systematic and comparative study that quantifies how much adsorbent is needed to achieve the level of residual phosphorus that is believed to permit physical refining. Such a study would allow local cost estimates to be made as a basis for selecting one of the options listed above.

On the other hand, if the oil to be refined has too high a phosphatide content for one of the above dry degumming processes to be economically attractive, another degumming/refining route has to be chosen, and this is where it starts to become difficult. There is the well-proven alkali refining process with its inherent neutral oil losses and effluent problems caused by the soapstock splitting process, but these problems are not universal. Formerly, most refineries in France had a soap works next door, and this took care of these problems. Nowadays some refiners sell their soapstock for a reasonable price, and this also solves their problems satisfactorily.

But what if there is no soap works nextdoor or soapstock cannot be profitably sold? Then the problems resulting from alkali refining may be considered to be too expensive to solve, and a degumming route that permits physical refining and thereby avoids soapstock splitting has to be looked into. As shown in Fig. 5.2, there is ample choice: various enzymatic degumming processes, acid refining, and water degumming followed by SOFT degumming. All of these processes allow physical refining and thus avoid soapstock.

Let's start by discussing the various enzymatic degumming processes. The main advantage of the enzymatic degumming processes is a yield improvement resulting from the conversion of phosphatides to gums that retain less oil and/or diglycerides that will finally be sold at refined oil value.In this respect, it offers an advantage over water degumming. Like water degumming, enzymatic PLC degumming does not touch NHP, and like water degummed oil, PLC degummed oil needs further treatment. I therefore regard the PLC degumming process to be a kind of alternative to the water degumming process, which is why I have put them into the same box in Fig. 5.2. This is also why they are primarily suitable for an oil mill. If this oil mill is not aiming to produce lecithin and is not vertically integrated into refining, it could increase its income by converting some of its phosphatides into diglycerides and selling them at oil value rather than meal value.

That leaves the question of whether this oil mill should treat its crude oil with PLC or water degum it, treat the gums with PLC, recuperate an oily phase that is rich in diglycerides, and sell this oily phase as such or after blending with the water degummed oil. The material balance is the same for both routes, so the choice depends on what these two routes cost. Is it cheaper to treat the oil with the enzyme or to treat the gums? I expect the gum treatment to be cheaper since the gum volume is only about 5% of the oil volume, and this should more than offset the cost of an additional treatment step.

As we know, the PLC Purifine® only catalyzes the hydrolysis of PC and PE and the gums also contain PI and the potassium salt of PA. How much oil do these latter phosphatides retain? Is it worthwhile to hydrolyze them with PLA or LAT and recover even more oil from the gums that way? That is something to be determined experimentally, and it is not unlikely that one company or another has already done so without publishing the results.

To me, it seems a bit of a waste to treat crude oil with PLC. Why not treat crude or water degummed oils with phospholipase A or lipid acyl transferase? From the above, it should be clear that all these enzymes do is catalyze the conversion of hydrated phosphatides to lysophosphatides. They do not act upon the NHP. To get rid of those NHP, an acid refining step has to precede the enzymatic treatment. On a laboratory scale with continuous high-shear mixing and a lot of patience, the enzymes may lead to a reduction in NHP, but on an industrial scale, they do not touch the NHP: The enzymatic degumming processes that have been promoted by the various enzyme manufacturers are nothing but "acid refining processes in disguise." That is why in Fig. 5.2, the box with the ACID REFINING process also mentions ACID REFINING PLUS ENZYMATIC PLA OR LAT DEGUMMING.

Even so, lysophosphatides retain less oil than their precursors, and this constitutes potential savings. This raises the question of how to realize these savings in the most economical manner. I don't know the answer, and as before, there probably is not a universal answer that is valid in all cases. Nevertheless, a bit of speculation can do no harm.

I have always disliked processes that are supposed to reach a multitude of goals. Alkali refining is supposed to remove both phosphatides and free fatty acids and lose a minimal amount of neutral oil. The same process is supposed to handle oils like crude soybean oil with a high concentration of phosphatides and a low FFA content as well as oils like palm oil having a high FFA content and hardly any phosphatides. The result is a mess. In principle, it is much better to have a process that aims to achieve just one thing. That allows the process to be optimized because there is a single goal. If a move gets you closer to that goal, continue; if not, go back. There is no conflict of interest.

Combining acid refining and hydrolyzing hydrated gums in a single process makes this process unnecessarily complicated. Decomposing NHP with a degumming acid can be achieved in a few minutes and requires a relatively small installation. Hydrolyzing gums enzymatically takes a fairly long time, so diluting these gums with, say, 30 to 50 times their volume of oil does not strike me as very sensible. It calls for a much larger installation than when the gums are hydrolyzed on their own.

Accordingly, I tend to opt for acid refining the oil and treating the gums separately. If these gums originate from oil that has not yet been water degummed, the gums contain PC and PE, and so exposure to PLC will liberate diglycerides that can contribute to oil yield. If these gums originate from water degummed oil, there is no point in treating them with PLC, but treating them with PLA or LAT will hydrolyze the phosphatides present in the gums so that some oil may be released and be recuperated. Which enzyme and how much enzyme have to be determined experimentally.

However, treating the gums with one or more enzymes is not the only way to recover their fatty constituents. In my Timothy L. Mounts Award address (Dijkstra 2010a), I recalled a paper published by Naudet et al. in 1954. In this paper, the authors report on the high-temperature hydrolysis of gums. This paper led me to pursue this approach, and I carried out some trials with J. De Kock. It turns out that gums can be hydrolyzed at a lower temperature than triglyceride oil and that on acidulation of the reaction mixture, a clear separation is attained between the fatty acids formed and the aqueous phase. There is no emulsion layer, as is often observed when soapstock is acidulated.

I also suggested a small, continuous unit comprising a high-pressure pump; a tubular reactor that heats the gums or soapstock to 220°C, provides the reaction mixture with a residence time of, say, 30 min, and allows heat to be recuperated; a cooling section; and a pressure relief valve. The reaction product would require some acidulation to recover the fatty acids but to a far less low pH than is necessary during soapstock acidulation. Accordingly, the neutralization of the aqueous effluent would be simpler. Its downstream effluent treatment plant should be able to cope with high COD effluent and precipitate phosphates. In addition to soapstock and/or gums, the unit could also process trap grease and perhaps even spent bleaching earth.

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Chapter 6
Neutralization

6.1 State of the Art in 1990

The annual production of edible oils and fats in 1990 was around 80 million tonnes. Twenty years later, this had more than doubled. Since almost all of this oil is also refined,[1] this implies that refining industry capacity also had to be doubled, but it does not mean that the capacity of all individual process steps has been doubled. There has been a shift from chemical refining, which is the subject of the present chapter, toward physical refining, which will be discussed in conjunction with the deodorization process in Chap. 9.

Chemical refining, also referred to as alkali or caustic refining, is the older of the two refining processes, so it is not surprising that in 1990, it was by far the major process. Only palm oil, lauric oils like coconut oil and palm kernel oil, and animal fats like tallow and lard were neutralized by physical refining. At that time, the successful development of adequate degumming processes in Europe made the physical refining of seed oils possible. The yield advantage of physical refining over chemical refining and the relatively high FFA content of the rapeseed oil and sunflower seed oil processed in Europe made it attractive to switch to the physical refining of seed oils. Moreover, this switch was encouraged by the fact that Europe still had quite a few stand-alone refineries and that discharging soapstock acidulation effluent became more and more difficult. Accordingly, the soybean oil these refineries purchased had already been water degummed and by physically refining that oil as well, they could do away with their soapstock treatment plant.

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[1] Refining means different things to different people. In the US, it is more or less synonymous with neutralizing, whereas in the UK, it covers the series of processes that lead to a fully refined oil, which in the US would be called RBD: refined, bleached, and deodorized. What it means outside the US and the UK is often far from obvious.

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4_6,

According to Blank (1942), a certain Schmersahl obtained a patent for refining cottonseed oil with caustic alkali in 1842. However, I did not manage to get hold of it through Google. Even so, we can assume that oils and fats have been alkali-refined on an industrial scale for about a century and a half. The process started with the batch or kettle process and evolved into continuous neutralization lines, and the total amount of oil that has been neutralized during this period amounts to several thousand million tonnes. Nevertheless, the process is poorly understood.

This lack of understanding is illustrated by the fact that the US and Europe use different neutralization processes: the Long Mix process in the US as opposed to Short Mix in Europe (Blake Hendrix 1990). Companies that operate refineries in the US and in Europe[2] are in a good position to compare the two processes and find out which one is better, but apparently, they have not done so since they continue to follow the local preferences.

A fundamental difference between the two processes concerns the use of degumming acid. When describing the two processes, Blake Hendrix (1990) provided their flow diagrams. The Short Mix process flow diagram shows the in-line addition of acid and its fine dispersion with a knife mixer. According to the flow diagram of the Long Mix process, no acid is added at all. In the Long Mix process, this addition is optional. As Erickson (1995) wrote, "The addition of phosphoric acid to crude degummed soybean oil in the day tank is a convenient method of pretreatment," but when he described the kettle refining process, he did not mention a degumming acid at all.

Perhaps the use of a degumming acid is superfluous. In 1971, Hvolby published a paper from which I have copied Table 6.1 here. This table lists residual amounts of phosphorus, magnesium, and calcium after the oil has been treated with an aqueous buffer of variable pH. It shows various things, including that the ratio of the residual magnesium to calcium contents hardly varies and that on an atomic basis, the sum of the residual magnesium and calcium contents is always less than the residual phosphorus content. This is in line with the current view that non-hydratable phosphatides (NHP) consist of calcium and magnesium salts of phosphatidic acid and also may contain some free phosphatidylethanolamine.

However, the main reason why I decided to copy this table is because its last line shows that at sufficiently high pH, all NHP are removed from the oil. That is presumably the reason why oil that has been neutralized by the Long Mix process without the prior addition of degumming acid can show a low residual phosphorus content.[3] What mechanism would be involved is anybody's guess. When discussing "questions that no one is asking" during my Chevreul Award address (Dijkstra

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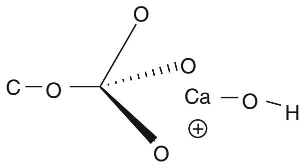
[2] These companies are generally referred to as ABC (Archer-Daniels-Midland, Bunge, and Cargill).

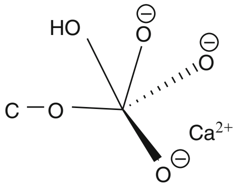
[3] When inquiring about this with people who have some experience with the Long Mix process, I learned that the residual phosphorus content is not measured on a routine basis and that it is not always negligible.

Table 6.1 Dependence of contents of P, Mg and Ca on pH of buffer solution (Hvolby 1971)

pH	P mmole/kg	Mg mmole/kg	Ca mmole/kg	Mg/Ca	(Mg + Ca)/P
"–1"	1.88	0.00	0.00	–	0.00
0	0.30	0.01	0.00	–	0.03
1	0.42	0.09	0.11	–	0.48
2	1.02	0.27	0.43	0.63	0.69
3	1.19	0.29	0.48	0.60	0.65
4	2.99	0.85	1.41	0.60	0.76
5	3.87	1.17	1.83	0.64	0.78
6	4.15	1.26	1.96	0.64	0.78
7	4.16	1.26	2.06	0.61	0.80
8	4.18	1.25	2.08	0.60	0.80
9	3.83	1.33	2.16	0.62	0.91
10	2.55	1.02	1.54	0.66	1.00
11	2.00	0.79	1.37	0.58	1.08
12	1.83	0.71	1.07	0.66	0.97
13	1.11	0.42	0.66	0.64	0.97
14	0.00	0.00	0.00	–	–

2010), I showed a condensed version of Table 6.1 and speculated about this mechanism.





The preceding figure shows the phosphate group in the NHP that is bound to a calcium ion. On the left-hand side, a hydroxyl ion attaches itself to the calcium ion; on the right-hand side, the hydroxyl ion is attached to the phosphorus atom. In both cases, the complex acquires a negative charge that is the likely cause of hydratability. In both instances, the oxygen atoms that are not linked to the glycerol carbon atom are to be considered equivalent in that charges rotate and that the hydrogen and calcium ions are not bound to individual oxygen atoms but form part of the complex.

Just imagine that we could rely on the caustic soda to get rid of the NHP. We would no longer have to disperse phosphoric acid into the oil and thus would no longer make calcium phosphate when this acid reacts with NHP. We would avoid the encrustation of the centrifugal separator disks with calcium phosphate and their regular, manual cleaning. In addition to saving on phosphoric acid, we could also save on caustic by having a water degumming step precede the neutralization (Charpentier 1991). In this water degumming step, we should try to minimize the oil content of the gums and not worry about the residual gum content of the degummed oil since the subsequent neutralization would take care of that.

We should finely disperse the caustic into the oil and use a knife mixer rather than a retention mixer (Blake Hendrix 1990) to ensure a complete reaction between the NHP and the caustic. I would guess that we could operate at Short Mix process conditions of caustic strength and temperature and thereby profit from the reduced viscosity of the oil at this high temperature. We would require less caustic since we would not have to neutralize the phosphoric acid. On acidulation, we would require less sulfuric acid, and the aqueous acidulation effluent would contain far less phosphorus.

Will it work? Perhaps it will. After all, according to Arutjunyan et al. (1988), treating water degummed[4] sunflower seed oil at 15–30°C with an amount of caustic soda that is equivalent to 5–20% of its free fatty acid content already removes all phosphatides. Has this been tried in a systematic manner? Perhaps it has, but I have not come across an article describing this approach. I would not be surprised if an attempt had been made and the results had been misinterpreted. So often experimental results are accepted at face value instead of being questioned because they are not in accordance with a preconceived idea or hypothesis. Anyway, it is a bit late now to start developing the caustic refining process.

Coming back to the state of the art, I cannot help but notice that globally, we neutralize a vast amount of oil, we use a large amount of reagents, we suffer from a steady oil loss by entrainment with the soaps, and we are faced with a messy soapstock treatment/disposal problem, so there is ample scope for improvement. What do we do about this? Hardly anything. The number of neutralization patents published over the last 20 years is embarrassingly small, far smaller than in previous years. Consequently, the present chapter will be quite short, which provides me with an opportunity to wonder why so little research is devoted to the neutralization process. Just compare neutralization with, for instance, extraction with supercritical carbon dioxide. Why does the latter, a non-starter because it offers no economy of scale, attract a lot of R&D attention while neutralization is ignored? These and similar questions have intrigued me for quite some time. I have even devoted editorials to this question (Dijkstra 2004, 2009), but I have not managed to arrive at a simple answer.

However, in the case of the neutralization of edible oils, there may be a likely answer: the scale of current industrial practice. I was confronted with the implications of an established scale of operations when still working for ICI on polyester polymer (PET). This polymer is further processed in spinning plants to make yarn and fibers, in film plants, and nowadays also in plants making parisons for bottle blowing. The polymer production is a two-stage process that starts with the production of what is commonly referred to as "monomer" but which, in fact, is a mixture of oligomers. This can be made from dimethyl terephthalate (DMT) and ethylene glycol by ester interchange[5] or from pure terephthalic acid (PTA) and glycol by direct esterification.

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[4] The specification talks about "hydrated vegetable oil" when meaning water degummed.

[5] In the edible oil industry, this reaction has a different name: "interesterification."

In the second stage, a polycondensation reaction converts this monomer into a highly viscous molten polymer by distilling off the excess of glycol. This reaction is carried out under vacuum[6] in an autoclave fitted with a very sturdy agitator and continued until the desired degree of polycondensation has been reached. The reaction is, in fact, a competition between the polycondensation that links chains together and the thermal cracking that chops them up again. A low vacuum favors the polycondensation without affecting the cracking, so maintaining this vacuum is very important.

I thought of a way to simplify this system by interrupting the polycondensation at an intermediate stage, shipping the resulting oligomer to the user plants, and completing the polycondensation there. I discussed this idea with the powers that be, and we agreed that, in principle, the idea would have a large number of advantages over current practice and could lead to a better and certainly cheaper product. It would require a fair amount of R&D though, not only on the actual polymer production but especially downstream. Carrying out this work on a large, full-size plant scale would be expensive and constitute a large risk. Doing it on a small, pilot plant scale would lead to insufficiently conclusive answers and producing on a small scale would not compete with the established scale of production. It would miss out on the economy of scale. So despite the idea's being considered quite attractive, nothing was done with it.

Something similar may also apply to the current neutralization process. A single line can now process some 600 t a day, and going to smaller lines makes the process more expensive. Therefore, developing the current process is not attractive to the aforementioned ABC since they operate on too large a scale. Small-scale operators or refiners processing niche oils are much better placed to carry out the required R&D on the neutralization process. However, the problem with small-scale operators is that they do very little R&D. Could a university cooperating with such a small-scale operator be the answer?

6.2 Neutralization Reagents

Sodium hydroxide (also known as caustic soda) is by far the most commonly used neutralization reagent in edible oil refining. However, since the 1990s, Daniels (1990, 1994, 2000, 2003, 2008) has pursued the use of potassium hydroxide. It has the advantage that the aqueous phase resulting from soapstock acidulation can be used as a raw material for plant fertilizer. If sulfuric acid is used for acidulation and the acidulation liquor is neutralized with ammonia, it contains N, P, K, and S. Another advantage mentioned is that the oil contained less soap. Plant trials (Hodgson 1995) led to the conclusion that "potassium hydroxide is a viable refining agent for soybean oil normally available in the United States and it can be used as an alternative to sodium hydroxide." Its benefits have also been the subject of a

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[6] That was my first confrontation with steam ejectors.

poster presentation (Gupta and McKinney 1999) that reported a 1% (absolute) lower refining loss for potassium hydroxide. The once-refined oil also contained less soap, so the wash water also contained less soap.

However, the same presentation also reported residual calcium levels of 15 and 12 ppm, respectively, for the sodium and potassium hydroxide–treated oils. Residual magnesium levels were 6 and 4 ppm, respectively. This means that the oil that had been neutralized with sodium hydroxide contained at least 20 ppm residual phosphorus and indicates that the Long Mix process is not always effective in removing NHP.

The use of calcium oxide as neutralizing agent has been disclosed by Myers (1997a, 1997b, 2000). The process intrigued me, so in 1998, I contacted the inventor to find out more about it. He asked me to try and raise some interest in his process, and this in turn led to some laboratory work at Ghent University that improved the process. The process has cost advantages in that calcium oxide is cheaper than sodium hydroxide, removal of calcium soaps by filtration is cheaper than removing sodium soaps with a centrifugal separator, and less oil is retained in the calcium soaps. Moreover, the process would avoid soapstock acidulation because the calcium soaps could be included in cattle feed as such and provide a bypass source of energy. Even so, there was little interest in the process, and it has not been applied industrially.

In 1992, Mukhopadhyay et al. reported the use of sodium metasilicate in a dry refining process for sesame oil. Mixing some sodium hydroxide with the silicate lowered the residual FFA of the oil. Solid alkali metal silicate, particularly sodium metasilicate pentahydrate, has been claimed by Canessa and Seybold (1994), but this application has not been pursued because of prior art (Jennings 1971). Silicate solutions have been used as agglomerating agent in a process in which contaminants including soaps agglomerate in a discrete phase that is removed by filtration. The granted patent (Hernandez and Rathbone 2002) does not include an example, and so it is not known to what extent NHP are removed. A subsequent application (Hernandez 2004) discloses the use of silicates as agglomerating agent during a kind of winterization process of an oil such as emu oil. Again, the document does not provide any analytical details of the resulting oil. According to Roa-Espinosa (2010), the use of a polymeric agglomeration agent also allows soap removal by filtration, but again, analytical details are lacking.

The use of aqueous organic nitrogen compounds such as, but not limited to, dimethylamino ethanol to extract FFA from acid triglyceride oils has been disclosed in Peter et al. (2000). More background information on the process is provided by Peter et al. (2001), but neither publication mentions what happens to the phosphatides.

Rice bran oil contains oryzanol (a ferulic acid ester), a compound with a free phenolic hydroxyl group that causes it to dissolve in aqueous alkali. To retain this oryzanol in the oil being neutralized, Lawton[7] et al. (2001) use a weak acid salt with a pH between 8 and 8.5 such as sodium, ammonium, or potassium bicarbonate.

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[7] The inventors work in academia. The front page of their patent contains a long list of “Other publications,” that is, non-patent literature, that is continued on the next page. The patent itself has some anomalies in that claim 30 should have been given number 31, vice versa, and then depend on claim 30 rather than claim 29.

By treating the neutralized oil with a strong base such as sodium hydroxide, an oryzanol concentrate is obtained.

Several inventors disclose the use of oxides for the neutralization of oils. The use of zirconia, alumina, hafnia, and titania is disclosed in an application (McNeff et al. 2008) whose main claim is so general and broad that I think it is unlikely that it will be granted as such:

> 1. A method for removing organic acids from a crude product mixture comprising: contacting the crude product mixture with a metal oxide substrate, wherein the organic acids in the crude product mixture bind to the metal oxide substrate, thereby removing free organic acids and forming a refined product mixture; and separating the refined product mixture from the metal oxide substrate.

Somebody must have reported having done so. Krumbholz et al. (2000), for instance, disclose a process "which is preferably carried out according to a chromatographic process, whereby aluminium oxide is used as adsorbent."[8]

In a subsequent patent application (McNeff et al. 2010), the same inventors also disclose a method to regenerate the metal oxide by rinsing it at elevated temperature with a fatty acid alkyl ester. All examples describe the removal of FFA from biodiesel. This explains why fatty acid alkyl esters are used in the regeneration step. Said step then only involves raising the temperature. It also explains why the patent does not mention what to do with the solution of FFA in the esters.

In 1985, UOP presented a poster (Gembicki et al. 1986) at the AOCS World Conference in Cannes to draw attention to their Sorbex process. They showed that they could separate oleic acid from triolein in an automated process of selective adsorption and desorption. Quite some time later, UOP applied for a patent (Priegnitz 1993) in which such a process is disclosed in detail. It employs silica gel as the adsorbent and a C_3–C_8 ketone, an ester, or ether as desorbent; this desorbent has to be recuperated from the product streams by evaporation. Good separation is reported between fatty triglycerides and FFA. By adjusting the feed rate, the diglycerides could be directed more to the triglyceride raffinate stream or to the FFA extract stream. No such direction is possible for the monoglycerides that ended up in the FFA stream.

6.3 Neutralization Processes Involving Organic Solvents

Whereas UOP only used a solvent to desorb the FFA from the adsorbent, Ayorinde and Hassan (1995) dissolve the oil to be deacidified in an organic[9] solvent such as isopropyl alcohol or hexane; their process can therefore be retrofitted into an extraction plant. They use aluminum oxide as adsorbent for the FFA and regenerate it by washing it with a dilute solution of sodium or potassium hydroxide.[10]

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[8] The phrase in quotation marks quotes the Abstract. The main claim is less specific and does not mention the "chromatographic process." Solvent-free chromatography is only mentioned in claim 3. This difference indicates the importance of studying the actual claims rather than just the abstract.

[9] I mean "organic" in the chemical sense, not in the agricultural sense.

[10] Alumina is amphoteric, so the oxide can dissolve in alkali to form an aluminate.

A patent application by Cargill (Eyal et al. 2009) discloses a process that treats the miscella that results from the solvent extraction process. This PCT application has a US priority date (06.06.08), but no US application has been published. It would have been interesting to compare the claims in the PCT application and the US application since in the former, the claims are multi-dependent,[11] which is not allowed in the US.

The miscella treatment process excludes the use of a centrifuge. This is novel, and so all kinds of process variants could be claimed on the strength of this novel element. The miscella can be concentrated or diluted and acids and/or bases and/or enzymes can be added. This makes me wonder if the non-patent literature does not somewhere describe a laboratory experiment in which a separating funnel was used to drain an aqueous solution from a miscella. The process claims to reduce neutral oil loss with the gums and/or the soaps, but the examples do not report on their oil contents. They do report residual phosphorus, and the only example where this is sufficiently low to permit physical refining is Example 6, in which an enzyme treatment is followed by neutralization with strong lye. Could it be that the latter is the cause of the low residual phosphorus content?

Bertholet (2003) has disclosed a neutralization process involving an alcohol such as ethanol or isopropanol. In this process, the oil is mixed with alcohol and then "titrated" with aqueous caustic. Adding the amount of caustic that is equivalent to the predetermined acidity is also a possibility. The alcohol contains relatively little water so that on acidulation with phosphoric acid, a precipitate of sodium phosphate is formed. On the other hand, the low water content of the alcohol increases its solubility in oil so that more alcohol has to be removed from the neutral oil.

The above process reminds me very much of the last R&D project I was actively involved with before leaving Vandemoortele. This project was inspired by an article on the use of membranes that led me to ask Wageningen University for a copy of a PhD thesis[12] (Keurentjes 1991). There I read that soaps dissolve in aqueous isopropanol (IPA), that oil does not dissolve in aqueous IPA and that less and less IPA dissolves in the oil with increasing water content. Then I remembered reading somewhere that during the extraction of oilseeds with IPA, phosphatides are extracted by aqueous IPA and oil is only extracted when the IPA contains very little water. Accordingly, mixing crude oil with alkaline aqueous IPA should lead to two phases, a heavy water/IPA phase also containing soap and phosphatides but no oil, and a lighter oil phase from which the FFA and the phosphatides had been extracted and containing a small amount of IPA – in other words, a perfect separation avoiding neutral oil loss during degumming and neutralization.

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[11] This means that dependent claims can depend on more than one previous claim. So they can start, for instance, with, "The method according to any of claims 1–19, wherein …" or "The method according to any of claims 1–10, 12–25, wherein … ."

[12] In the Netherlands, it is customary to have a PhD thesis printed and to send copies to colleagues, family, and friends together with an invitation to its public defense and the subsequent reception. The laboratory where the work was done retains a number of copies for future distribution, so getting a copy was no problem.

Some experimental work was carried out and looked promising, but then the project[13] was killed by management, who had applied some kind of evaluation procedure. Instead of concluding that IPA losses would affect the profitability of the process and that controlling these at a low level should therefore be a research target, it just assumed a loss of a certain percentage and concluded that the process was not profitable. So the work was stopped, and aspects where the solvent loss was less important such as the deoiling of lecithin or oil recovery from soaps were not pursued either. Much later, in 2003, Bertholet also used an alcohol such as ethanol or isopropanol or a polyol, such as propylene glycol, glycerol, or polyethylene glycol, to mix with the aqueous alkali. He reports the solubilization of the soaps in the aqueous phase and also observes a much reduced neutral oil loss. The polyols in Bertholet (2003) have the advantage of not being volatile, which may cut losses and certainly avoids the necessity of having an explosion-proof plant.

Such a polyol (polyethylene glycol, PEG) is also what Peter et al. (1998) used in their purification process. They noted that free fatty acids divide themselves between the oil phase and the PEG phase, thus enabling a countercurrent extraction process. So their process differs from the approach outlined above in that the PEG is anhydrous, does not contain alkali either, and requires a countercurrent extraction column. Purifying the PEG is also not that straightforward. It is therefore not surprising that the application (Peter et al. 1998) was not pursued. However, I think that combining the findings of Keurentjes, Bertholet, and Peter with the internal Vandemoortele observations might well lead to an elegant approach to oil purification.

Another application mentioning glycerol is Keskinler et al. (2008), which claims priority from an application in Turkey. The English of the PCT application is difficult to understand, but I gather that alkaline alcohol is used when the resulting neutral oil is to be used for biodiesel and that alkaline glycerol is used for food applications since this avoids the formation of fatty acid methyl or ethyl esters. In both cases, glycerol is added to wash the reaction mixture and remove the soaps. The Search Report lists three documents, each of which is given an X, so that it is not surprising that the application did not enter the European phase.

An application filed by a membrane manufacturer (Boam and Lim 2010)[14] discloses a neutralization process in which the oil to be neutralized is extracted with a solvent such as ethanol. This leads to an oil product phase that is substantially depleted in free fatty acids and a solvent phase containing the extracted free fatty

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[13] Like most of our R&D projects, this one had an acronym: DON'T WAIT, or *Degumming Or Neutralization? Try Water-And-Isopropanol Treatment*.

[14] The US application has been assigned to the Norwegian company Due Miljø AS and the British company Membrane Extraction Technology Ltd. Earlier applications like GB 2 4441 132 were made by the Norwegian company Pronova Biocare AS, a subsidiary of Norsk Hydro. This illustrates that patents can change hands even before having been granted.

acids and some of the glycerides. The solvent phase is then processed with a membrane to recover the glycerides.[15] Similarly, oil can be deacidified by methanol extraction, whereupon the extract can be concentrated by membrane filtration (Kale et al. 1999). Deacidification of oil dissolved in acetone by membrane separation has also been reported (Zwijnenberg et al. 1999). The permeate consisted almost entirely of fatty acids in acetone, and only small traces of triglycerides were found.

6.4 Neutralization Processes by Esterification

Crude shea butter tends to have a fairly high FFA content. Because the oil is to be used in confectionery applications, interesterification has to be avoided. Since this may happen during physical refining, the oil is preferably alkali-refined, but this leads to neutral oil losses on alkali refining, and moreover, the resulting neutral oil contains appreciable amounts of partial glycerides. These affect the crystallization behavior of the oil during subsequent fractionation and of the stearin fraction obtained by this fractionation process and used as a cocoa butter equivalent (CBE) component. So Pieter Maes and I had the marvelous idea of killing two birds with one stone by developing what we called "deacidification by re-esterification."[16] If we were to esterify the partial glycerides in the shea butter with fatty acids, we would increase the neutral oil yield and improve the crystallization by decreasing the partial glyceride content.

This idea differs from the deacidification processes by re-esterification as reported by Andersen (1962) and recently disclosed again (Zeng et al. 2008). In these processes, glycerol is added to the oil in order to have an excess of free hydroxyl groups over FFA so that when the residual FFA level decreases, there are still free hydroxyl groups present and the reaction continues. We added FFA and thereby maintained a free carboxyl group concentration that was higher than that of the free hydroxyl groups, esterified to a low residual partial glyceride content, and then removed the excess of FFA to arrive at a neutral oil with a low partial glyceride content.

Like Zeng et al. (2008), we also needed a catalyst to speed up the esterification reaction. Zeng et al. use zinc oxide, which is cheap and has a low toxicity. However, they do not mention that it also acts as an interesterification catalyst, which may be all right for their rice bran oil but is disastrous for a CBE precursor. We also used bleaching earth; its acidity catalyzes the esterification and thereby allows low-residual partial glyceride levels to be attained. It also has the advantage that the

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[15] The same company (Due Miljø AS) is mentioned as assignee in a patent application describing a process in which oil is mixed with an adsorbent and then recovered by membrane filtration (see Berge et al. (2010) in Chap. 7).

[16] This is a literal translation of the Dutch term *Herveresterende ontzuring*, which is more compact. It can also be called "remediation" (Cowan 2011).

catalyst can be removed by filtration. Sadly enough, the acid bleaching earth also catalyzes the formation of *trans* isomers at esterification temperatures, which rules out its use for CBE precursors.

Perhaps we should have tried using enzymes. Their use in deacidifying oils has been disclosed by Gutsche et al. (2003), who set out to utilize high-acidity oils in biodiesel manufacture. Accordingly, they add a lower alcohol to the acid oil and pass the mixture over an immobilized lipase. De Greyt et al. (2008), on the other hand, add one or more polyhydric alcohols (such as glycerol) and a lipase that catalyzes the esterification of the FFA and the glycerol and then remove residual FFA by steam stripping. In this way, they utilize a high-FFA oil as raw material for biodiesel production. The use of lipase enzymes as catalyst in the deacidification of fish oil and palm oil was the subject of a presentation (Cowan 2011) that also discussed means of water removal to drive the reaction toward the ester side.

6.5 Miscellaneous Neutralization Processes

Standard neutralization processes using caustic soda lead to the formation of soaps. These are removed by centrifuge to produce a neutral oil with residual soaps. These soaps can then be removed by a dilute alkali wash followed by one or two water washes.[17] These washes lead to soapy water that cannot be discharged as such. The use of silica hydrogel obviates these washes, as explained by Welsh et al. (1990).[18] A slightly more recent patent (Welsh and Bogdanor 1993) discloses the "modified caustic refining process," starting the main claim with a preamble describing the prior art, which includes a washing step. Then the claim continues by disclosing THE IMPROVEMENT COMPRISING the silica treatment; finally, it concludes by eliminating the washing step from the preamble and concluding that the formation of a dilute aqueous soapstock is avoided.

We pursued similar objectives when developing the TOP degumming process. It is therefore not surprising that we applied some of our findings to the neutralization process. Thus, the use of two centrifugal separators in series, whereby the first ensures a minimum oil content of the gum stream and the second one ensures a highly purified oil stream and recycles its gum stream (Van Opstal et al. 1990), was transferred to the neutralization process (Dijkstra et al. 1994). The addition of wash water to the oil stream leaving the first separator and recycling this from the second separator to the oil stream being fed to the first separator (Cleenewerck et al. 1992) was also transferred to the neutralization process (Muylle et al. 1994). When Vandemoortele sold its refineries, these applications were not pursued. They were

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[17] Carrying out these two water washes countercurrently saves on water and thus also on effluent treatment.

[18] This article also has a long list of patents, presentations, articles, and brochures describing the use of Trisyl®.

quoted, though, as prior art for a subsequent application doing something rather similar (Kellens and Schols 2009); this was therefore withdrawn.

There are also a number of patents and patent applications that deal with the neutralization of specific oils. Accordingly, Melin[19] (1991) purifies olive oil by neutralizing the oil in an inert atmosphere with an excess of a saturated solution of sodium carbonate. Subsequently, he washes the oil with water, dries the washed oil, and bleaches the dry oil under an inert atmosphere. The resulting oil is no longer virgin (let alone extra virgin), but olive oil refined according to Asbeck (1992) retains this qualification since all this process involves is filtering the oil through a microfilter. High-acidity olive oils, which are therefore not virgin, can be refined with an improved yield by first removing most of the free fatty acids by vacuum stripping and only then treating the oil with lye. According to the process disclosed by Lal Ganguli and Van Putte (2001), the oil then has to be bleached and deodorized.

Crude neem oil has a high sulfur content. Its miscella can be purified by washing it with an aqueous alkaline solution of hydrogen peroxide that may also contain an alcohol (Lidert 1994). The treatment is not very effective since it still contains several hundred ppm of sulfur, and subsequent hydrogenation of the oil still required 2% by weight of standard nickel hydrogenation catalyst. The claims of US patent (Selder 2003) are a nice illustration of how the number of claims increases if multi-dependency is not allowed. The main claim is a product claim (linseed oil) on which the two subsequent claims depend. Instead of having a process claim saying, "A process for the manufacture of a linseed oil according to claims 1 to 3 . . .," there are three almost identical claims that depend on claims 1, 2, and 3, respectively. Process variants have to be formulated in triplicate as well. The process and its variants are not remarkable, except for the patent mentioning the use of manganese tetraborate as an agent that prevents thickening of the oil and can act simultaneously as a drying catalyst.

According to Bijl and Wolf (2002), a purified pufa oil mixture containing ω-3 and ω-6 oils is prepared by mixing an ω-3 oil with an ω-6 oil and purifying the mixture. In a subsequent claim, the oils concerned are specified as single-cell or microbial oils. The Search Report contained two documents with an X, and in Europe, the application is "deemed to be withdrawn." Now we come to the granted patent I have saved for the last (Lee et al. 2001). It is concerned with refining fish oil and the treatment comprises, among other steps, the preparation of a mixture of fish oil and water containing monosodium glutamate, the fermentation of this mixture in the presence of urea, and, would you believe it, mixing the oil with earthworm excrement.

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[19] In Europe, the patent was applied for in 1997 and granted in 1991. Within the priority year, an application (04/222,810) was filed in the US. This was abandoned but continued as application (07/562,413) in 1990. This was again abandoned and continued as application (08/121,663) in 1993. Finally, the patent (US 5,962,056) was granted in 1999, 8 years after the patent had been granted in Europe.

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Chapter 7
Bleaching

7.1 State of the Art in 1990

When presenting a paper about bleaching in 2002, I quoted Prof. M. Naudet (1965),[1] who complained about the lack of insight into the bleaching process by writing, "The bleaching of oils and fats is probably the least understood stage in the refining of fatty materials." Given the sorry state of insight into the neutralization process highlighted in the previous chapter, the understanding of what happens during the bleaching process may well be next to nothing.

During this presentation, I illustrated this lack of insight by quoting three different mechanisms that had been put forward to explain the removal of soap during bleaching. Newby (1947) regarded the bleaching earth as a kind of filter aid for the solid soap particles since he observed the same low residual soap content when using bleaching earth and a filter aid. On the other hand, Taylor (1993) shows a number of graphs in his review article that indicate lower residual color levels when the oil contains less soap, which could indicate a kind of competition between coloring compounds and soap; this favors soap removal by adsorption. The third mechanism (Arbeitskreis's "Technologien der industriellen Gewinnung und Verarbeitung von Speisefetten" 1993) suggested that soaps are acidulated by the acid sites on the activated bleaching earth and are not removed but converted into free fatty acids. Much later, I read in Inturrisi (2007) that according to Bernardini (1985), "The acidity of the earth has the effect of increasing the FFA content of the bleached oil by approximately 0.1% for each kg of earth used for bleaching 100 kg of oil." However, most of this turned out to be incorrect since experiments at ITERG,[2] Pessac, showed that the acidity of oil containing soaps did not alter on bleaching (Dijkstra 2002).

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[1] The article itself is in Italian, but the French abstract starts with, "Le blanchiment des corps gras par les terres ou noirs décolorants est très probablement le stade le plus mal connu du raffinage des corps gras ...."

[2] ITERG is the French Institute for Oils and Fats.

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4_7,

There is no acidulation, and consequently, a combination of adsorption onto the earth and the earth acting as filter aid is likely.

This lack of insight is also reflected in journal articles. When authors measure a change in oil color, they still tend to use Lovibond®[3] units instead of the oil absorbance, although the latter has the advantage of being proportional to the concentration of the compound responsible for the color. Moreover, rarely do authors correct the oil color as measured for the coloring matter that is not removed by bleaching. Thirdly, color reduction need not solely stem from adsorption by bleaching earth; it can also result from a thermal breakdown of coloring compounds: heat bleaching. When studying the bleaching process, this heat bleaching should be taken into account by carrying out a reference experiment without the adsorbent; hardly anybody does.

Surveying the patent literature reveals a number of patents that originate from bleaching earth manufacturers and that disclose production methods for bleaching earths and/or bleaching earth with specific properties. These patents fall outside the scope of the present monograph. This also holds for patents disclosing methods to clean used frying oil by treating it with an adsorbent. If patents assigned to a bleaching earth manufacturer also disclose a specific bleaching process, I cannot but discuss them. This also holds for several patents dealing with silica adsorbents and their use in edible oil processing.

In fact, the initiative by W.R. Grace & Co. to enter the edible oil processing industry with its silica adsorbent Trisyl® initiated a fair amount of innovation in what had until then been a rather stagnant field. This chemical company had to familiarize itself to some extent with the edible oil industry, and since I had worked in the chemical industry, people from Grace found it easier to talk to me than to people who had been working with oils and fats all their lives. I could look at the industry as an outsider and explain it from the inside. When I explained to them that I had saved a lot of laboratory time when developing the TOP degumming process by using an ICP emission spectrometer for determining trace elements in oils (Dijkstra and Meert 1982),[4] they were quick to adopt this analytical method (Kassa and Bogdanor 1987), whereas the Crosfield Group still used graphite furnace atomic absorption spectroscopy in 1994 (Nock 1994b).

7.2 Synthetic, Silica-Based Adsorbents

To provide a proper overview of the development of synthetic, silica-based adsorbents, I must start in 1986, when the first patent (Welsh and Parent 1986b) was published.[5] It discloses a process for the removal of trace contaminants from glyceride

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[3] The Lovibond® color measurement was developed for judging beer without drinking it by Tintometer Ltd., a company that was founded in 1885 by Joseph Lovibond, a prominent brewer.

[4] It is, of course, very gratifying to me to see that this method has since become widely adopted.

[5] The priority date of this patent is 7 December 1984, and it was granted on 16 December 1986, which is only 2 years later. I would guess that W.R. Grace & Co. asked for speedy treatment.

oils by treating them with an adsorbent that consists of an amorphous silica. A subsequent claim specifies that the water content of this amorphous silica is at least 30% by weight; the commercial product Trisyl® contains some 65% water.

At the same time, the European application (Welsh and Parent 1986a) was also published with a Search Report showing quite serious prior art. So I had a look at the granted European patent and saw that, indeed, the main claim is totally different from the main claim in the application and the patent as granted in the US; the number of claims granted in Europe is also quite a bit smaller.

It is therefore not surprising that the examination in Europe took quite some time: The granted patent was not published until early 1992. Then the 9-month opposition period started; both Laporte Industries Ltd., UK, and Süd-Chemie AG, Germany, filed an opposition. After oral proceedings in 1994, the opposition was rejected, but an appeal against this decision was filed. Another hearing was held in 1999, where the appeal of the opponent was also rejected. So it took 15 years from the priority date to sort this out. It also indicates the importance W.R. Grace & Co. and its competitors attach to the use of silica hydrogel in treating edible oils. This importance is also shown by the fact that this company was invited to present a paper (Welsh et al. 1990) at the AOCS World Conference held in Maastricht.

The main claim in the European application is quite broad in that it describes a treatment with an adsorbent that is described as “comprising a suitable amorphous silica.” The main claim granted in the US describes the adsorbent as “consisting of an amorphous silica which has an effective pore diameter of greater than 60 Ångströms,” whereas the granted European patent defines the average pore diameter (APD) as a function of pore volume and surface area. This illustrates that examination may cause the same invention to be defined differently in different countries.

The next evolution in the use of silica was to treat it with an acid. At first, only organic acids were used (Parker and Welsh 1988), but a few months later, a patent was applied for that also disclosed the use of inorganic acids and specified the acid strength as having a pK_a of 3.5 or lower. This application[6] led to two US patents, one covering the process (Pryor et al. 1988) and the other (Pryor et al. 1989) covering the product used in the process. A slightly earlier application (Welsh 1989) disclosed the use of partially dried silica hydrogel in removing contaminants from oil and also claimed an increase in contaminant adsorption capacity as a result of an acid treatment of the adsorbent.

As mentioned in Chap. 5, Sect. 5.5, Joseph Crosfield & Sons, an important manufacturer of silicates, was part of Unilever at that time. Consequently, Unilever opposed one of the Grace patents and also filed its own applications (Van Dalen et al. 1990), which in the US led to the patent (Van Dalen et al. 1993). The Search Report of the European application[7] lists three documents considered to be particularly relevant, but even so, the claims in the granted patent are as filed. Not surprisingly, Süd-Chemie AG filed an opposition in 1996, but it was rejected in 1999.

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[6] The application date was 15 May 1987, so, again, examination took very little time.

[7] This report was published separately as an A3 document in 1991.

Another approach by Unilever was to synthesize adsorbents. Staal et al. (1989) disclosed how to make a calcined metal oxide–silica adsorbent that can be regenerated without substantial loss of activity. The calcination conditions used for the regeneration are 1 h at 700°C, and its use in bleaching led to the same results. Surprisingly, there is no claim specifying this regeneration, and the corresponding process patent (Staal et al. 1990) does not specify this regeneration either. The manufacture of a synthetic, macroporous alumina silica is disclosed in (Lammers and Groeneweg 1990), and this product is also calcined before being used. It can also be regenerated, and one or more claims are devoted to the recycling of regenerated adsorbent. The calcination temperature of the regeneration process is 650–800°C.

Since Unilever was working on adsorbent regeneration, W.R. Grace did so too and disclosed a silica alumina adsorbent "to be repeatedly thermally regenerated by calcination to retain a high capacity for the removal of chlorophyll" (Bogdanor and Welsh 1993).[8] Not surprisingly, the Unilever applications were quoted as prior art and Grace withdrew its European application. I am not aware that any of these synthetic adsorbents were ever commercialized.

However, in the early 1990s, the future lack of commercialization was far from obvious. Consequently, bleaching earth manufacturers, keen to safeguard their future, not only opposed patents but also applied for patents disclosing synthetic adsorbents to be used in edible oil processing. Laporte Industries disclosed a zirconium phosphate (Taylor et al. 1992a)[9] and an organoclay adsorbent in which onium cations such as phenyltrimethylammonium occupy at least some of the cation exchange sites (Taylor et al. 1992b). The organic constituents provide the adsorbent with affinity for polyaromatic hydrocarbons (PAHs) like benzo(a)pyrene. Süd-Chemie also disclosed a synthetic adsorbent in the form of a polysilicic acid that contains the oxides of at least two metals with a valency of at least 2, one of which is iron and the other aluminum (Schall et al. 1998).

Because silica hydrogels were something novel, they were given intensive marketing support. Part of the marketing effort was publicity: journal articles giving background information (Chapman et al. 1994; Chapman 1994; Parker 1994) and oral or poster presentations at conferences (Nock 1994a, 1995). Despite the intensive marketing effort promoting these silica adsorbents, it took time for them to get any foothold in edible oil processing. In Europe they started being used for olive oil since the lower silica dosage reduced oil loss and the high price of olive oil justified the expense of the silica. In the US, silica hydrogels were used in the so-called modified caustic refining process (Welsh and Bogdanor 1987) to eliminate a water-washing step of alkali-refined oil.[10] The silica did remove soaps and phosphatides,

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[8] This application belongs to a family (AU, BR, MX, ZA) that does not include the US. At that time, the US did not yet publish applications, so we do not know whether or not Grace also applied in the US. I would expect so and conclude that no patent was granted or the application was withdrawn, as in Europe.

[9] Laporte Industries sold its bleaching earth business to Kohlberg Kravis Rogers in 2000, but prior to that it decided not to pursue this application or the next.

[10] See also Sect. 6.5.

but color removal was a problem. This was solved in a number of ways. A simple treatment is sequential. The first treatment is with amorphous silica; this is removed and the filtrate is then treated with bleaching earth. This process has been disclosed by Price (1991) for treating wax esters.

According to Van Dalen and Brunia (1991), mixing silica hydrogel in oil and then drying the oil locks the soaps and phosphatides inside the shrunken pores of the hydrogel and eliminates competition for the active sites of the bleaching earth that is added subsequently. On the other hand, Pryor et al. (1994) first treat the oil with amorphous silica and then pass the oil through a packed bed of "a pigment removal agent," which is "a natural or synthetic silica alumina material …" (claim 21) or "acid-activated or non-acid-activated bleaching earth or clay" (claim 23).

In 1993, Denton disclosed a process for the removal of contaminants with a "porous amorphous silica hydrogel support that has been treated with a base in such a manner that at least a portion of said base is retained in at least some of the pores of the support to yield a base-treated hydrogel adsorbent containing about 30–80% water." This patent is one of a family of nine that includes a European application that did not result in a granted patent. So I decided to *View the document in the European Register* and saw to my surprise on 9 February 1995 a "Dispatch of communication of intention to grant (Approval)," followed on 20 June 1995 by "Application refused. Date of legal effect [1995/50]," and on 18 July1995 by "Dispatch of communication that the application is refused. Reason substantive examination." This made me quite curious, so I tried to consult the file wrapper by clicking on *All documents,* but to no avail: **File No EP92105272**[11] **has been destroyed and is therefore no longer available for scanning.** So although the above tells me that the European Patent Office can reverse its earlier decisions, I will never know why it did so in the present case.

PQ Corporation, the current owner of what once was Joseph Crosfield & Sons, disclosed a process to make a silica xerogel (Canessa and Brozzetti 2001), which I gather is a hydrogel with somewhat less water. The product described in the examples has a water content of only 12%. Further process developments were also disclosed in patents and patent applications (Estes et al. 1995a; Leake 1997a, 1997b; Nock 1996; Owen 1997).

A remarkable process is the *modified physical refining* (MPR) process (Toeneboehn et al. 1994), which can be regarded as the opposite number of the *modified chemical refining* (MCR) process (Welsh and Bogdanor 1993). In the latter process, a silica hydrogel treatment replaces the water wash that follows the soapstock removal in the caustic refining process. Since this caustic refining process also removes phosphatides, the MCR process mainly aims at the removal of residual soaps. The MPR process, on the other hand, must be regarded as a kind of dry degumming process in that it aims at the removal of phosphatides. It is based on the synergy observed between soap and phosphatides removal. Accordingly, providing soaps by adding a small amount of lye to the oil to be dry degummed facilitates the removal of phosphatides from that oil, and these include non-hydratable phosphatides

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[11] This is the number given to the application concerned.

Table 7.1 Properties of water degummed soybean oil after various treatments

Treatment	P ppm	Ca ppm	Mg ppm	Fe ppm	Soap ppm	ChlA ppm	Color R	Color Y
Water degummed oil	88.1	43.1	24.1	0.6	-	0.40	15	70+
After NaOH addition					519			
Trisyl® 300 silica	1.7	0.7	0.4	0.0	0	0.37	13	70+
Clay bleached	0.5	0.5	0.2	0.0	0	0.02	4.8	70+
Deodorized	0.6	0.5	0.1	0.0	0	0.00	0.2	1.6
Control Trisyl® 300 silica	25.4	15.2	8.0	0.2		0.38	18	51

(NHP). To illustrate this remarkable finding, I have copied Table II from (Toeneboehn et al. 1994) as Table 7.1.

This table shows that treating the water degummed soybean oil containing 88.1 ppm of residual phosphorus in the presence of soaps with 1.5 wt% Trisyl® 300 silica removed all the NHP. Without the soaps, most NHP were also removed by that amount of Trisyl®, but it still left 25.4 ppm of residual phosphorus. So whereas Nock (1993) treats his NHP with an acid and adsorbs the phosphatidic acid that has been dislodged from the NHP, Toeneboehn et al. adsorb the NHP as such and use/need soaps to do so. The cost of using 1.5 wt% of silica is prohibitive, and the patent does not indicate how much phosphorus would have been left if less silica had been used. Lower amounts are used in other examples, but then, the NHP content of the oil was also much lower; besides, the examples also show that lower residual metal contents result when the oil has been pretreated with a degumming acid. So which process a refiner should adopt is not clear from the literature data, and the fact that the MPR process is no longer mentioned may well provide the answer the literature does not provide. Nevertheless, the observation that soaps encourage silica to adsorb NHP is most intriguing.

Apparently, this soap is not necessary when using vast amounts of silica hydrogel. Delmas and Walsh[12] (2001), Walsh and Delmas (2000) use about 20% by weight of silica in a column and also reduce the FFA content of their crude oils to such an extent that further removal is no longer necessary. They do not mention deodorization, but this could be advisable for seal oil. The large amounts of spent silica resulting from their process are used as a feed ingredient.

Another patent issued the same year (Toeneboehn and Welsh 1994) discloses the use of silica hydrogel for the removal of sulfur from oils to be hydrogenated. In this patent, the *Background of the invention* refers to an article (Cho-Ah-Ying and de Man 1991) that describes the use of Trisyl® that had been activated by heating at 240°C for 3 h. The inventors therefore provide experimental evidence showing that their process using a silica hydrogel containing at least 25 wt% water (claim 1) performs better than the dried silica hydrogel. Accordingly, a patent was granted within 2 years of filing.

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[12] One of these patents gives his name as Walsh, George **R.** and the other as Walsh, George **E.**

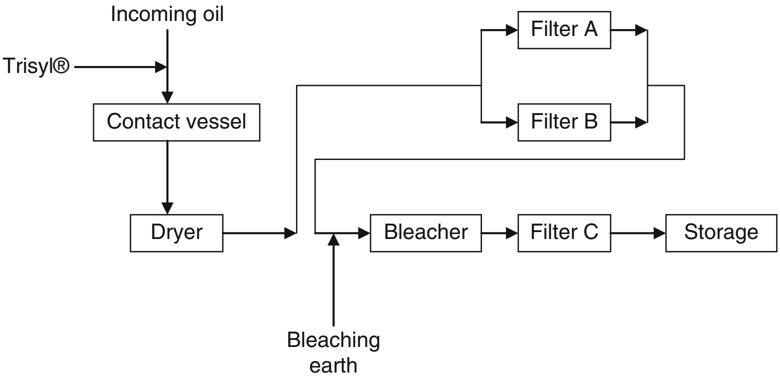

Fig. 7.1 Staggered filtration system (Jalalpoor 2008)

Yet another patent assigned to W.R. Grace & Co. (Estes et al. 1995b) is concerned with the problem that adsorbed soap appears to leach out of the amorphous silica adsorbent in the vacuum bleacher. The problem could be solved by removing the silica adsorbent with the adsorbed soaps from the oil before the latter is sent to the vacuum bleacher, but the patent discloses a better method: drying at least part of the oil before adding the silica adsorbent. Reading this patent made me wonder why W.R. Grace had deemed it desirable to file this patent with 12 different Patent Offices; that is quite a costly affair. Moreover, it would be very difficult to police this patent and prosecute refiners who buy silica hydrogel from the competition. I think that this patent was simply a matter of waving the flag and that could also explain why the application in Europe was withdrawn despite its promising Search Report. Another reason could be to prevent the competition from obtaining a similar patent by creating prior art, but that would have been achieved by a single application provided it was published.

The last application originating from W.R. Grace (Jalalpoor 2008)[13] that I want to discuss aims at fully utilizing the bleaching capacity of the bleaching earth. As I explained in 2002, spent earth that has been in contact with bleached oil still has bleaching capacity for the treatment of non-bleached oil. This is the basis of the Öhmi countercurrent bleaching process (Transfeld 1994) to be discussed in the next section and is also utilized in the staggered filtration system that has been shown in Fig. 7.1.

In a first stage, the oil to be bleached is treated with silica hydrogel and dried. The silica adsorbs the phosphatides but leaves the chlorophyll (or pheophytin). Therefore, the second stage involves the removal of this coloring compound with bleaching earth by pumping the suspension of silica in oil to a filter containing bleaching earth and removing the coloring compounds in a kind of chromatographic manner. The oil leaving the filter is then mixed with fresh bleaching earth and sent to another filter that is empty to start with and gradually fills up. When it is almost full or when the oil leaving this filter is insufficiently bleached, filters are switched

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[13] In comparison with earlier applications, this one is much more difficult to understand. Different author?

so that this filter becomes a chromatographic filter. The filter that was previously used in a chromatographic manner is emptied and allowed to fill with bleaching earth by being connected to the bleacher.

This staggering process aims at approaching the adsorption equilibrium between bleaching earth and non-bleached oil. As explained on theoretical grounds (Dijkstra 2007a), the color loading of the bleaching earth at this equilibrium is much higher than when the earth is in contact with bleached oil. Consequently, the process reduces the bleaching earth requirement to arrive at a specified bleached color. Normally, pumping non-bleached oil through a filter containing bleaching earth will tend to cause colmatation. However, the particle size distribution of commercial silica hydrogel products to be used in oil bleaching is such that they act as filter aid, so that pumping a suspension of silica in non-bleached oil to such a filter will prevent it from clogging up.

Silica hydrogel can also be advantageously used in the refining of fish oil and seal blubber (Mag 2007). Contacting the oil with silica hydrogel, then contacting it with bleaching earth, removing the adsorbents, and then stripping the oil under vacuum leads to a bland oil that can be used as a nutritional supplement and avoids alkali refining. A colloidal silica is used to purify oil in the process according to Brems et al. (2009). It is removed from the oil by centrifuge before the oil is bleached with bleaching earth.

7.3 Processes Using Other Adsorbents

Whereas silica hydrogel effectively removes soaps and phosphatides from the oil, bleaching earth is required to adsorb chlorophyll and its breakdown products. However, there are also other ways of removing these compounds. Beharry et al. (1994) dispersed phosphoric acid in the oil containing these compounds, and maintained the dispersion at a temperature of 70–150°C and a pressure below 10 mmHg until a precipitate containing chlorophyll color impurities was formed. Another way to get rid of chlorophyll is by using an enzyme: chlorophyllase (Lam et al. 2006).[14] The enzyme can be immobilized onto silica and decolorize "vegetable oils including oils processed from … oil fruits, such as palm oil."[15]

But why bother with adsorbents or enzymes at all? According to Unilever (Brunia et al. 1996),[16] a refining process comprising the steps of degumming the oil, heating the oil under vacuum in the absence of adsorbents, removing unwanted components,

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[14] I did not print this application since it has 237 pages and lists 238 claims. The Russian family member even has 322 pages.

[15] Such remarks are typical of companies (Diversa/Verenium) and/or patent agents who want to play it safe by including all eventualities; in doing so, they betray their ignorance or lack of familiarity with the subject.

[16] The only other family member of this application is an Australian one, and that was not pursued.

Table 7.2 Adsorbent properties and residual oil color (Ibuki et al. 1993)

	Activated clay properties			
Example No	Specific surface area (m^2/g)	SiO_2 content (wt %)	Fe_2O_3 content (wt %)	Red color intensity
Ex. 1	283	79.8	1.9	7.1
Ex. 2	255	78.3	2.3	7.5
Comp. Ex. 1	280	**65.0**	2.3	**14.2**
Comp. Ex. 2	293	**92.4**	2.8	**15.3**
Comp. Ex. 3	**400**	72.4	2.6	**15.2**
Comp. Ex. 4	**200**	76.8	2.4	**12.0**
Comp. Ex. 5	292	86.3	**5.9**	**13.0**
Comp. Ex. 6	**175**	**61.5**	**6.0**	**14.1**
Mixture	**180**	**62.4**	**5.8**	7.8

and deodorizing the oil "may yield an oil with an acceptable color." Another Unilever patent application disclosing a bleaching process for olive oil (Decio and Van Oosten 1992)[17] also claims "an edible oil comprising 50–90% oleic acid residues and less than 0.4 mg/kg chlorophyll or degraded components thereof." Claims like that are speculative. Of course, the inventors must have known that well-bleached canola oil, which contains some 60% oleic acid, could be cited as prior art by the Examiner or during an opposition but only if somebody had published the chlorophyll content of such an oil before the priority date.

In a patent granted to Fuji Oil Co. (Ibuki et al. 1993),[18] the properties of an effective bleaching earth have been specified in accordance with experimental evidence in Table 1, which I have given here as Table 7.2.

In this table, values that are outside the specification of a specific surface area of 250–350 m²/g, an iron oxide content of 1.5–3.0 wt%, and a silica content of 70–90 wt% have been printed in bold. However, as shown in Table 2 of the patent that has been used to arrive at the last row of our Table 7.2, using a mixture of 5% of the clay used in Example 1 and 95% of the clay used in Comparative example 6, which has properties outside the specification, also yields a low red color value. So the patent itself suggests how to circumvent it: Use the mixture.

To me, this patent (Ibuki et al. 1993) illustrates a dilemma that we face regularly as inventors: Should we delay our application until we have more insight into what we are talking about, or should we already apply for a patent when we hardly understand what makes our invention work? Waiting entails the danger that the competition may file before we do. When applying early, there is the danger that a reader of our application understands why it works and can then formulate a patent of his own claiming what is essential. Insight into what makes the invention work, into its

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[17] This is the only publication of this application, which was subsequently withdrawn. Should it therefore be regarded as a creation of prior art preventing the competition from claiming something similar?

[18] The colorimeter used in this patent is made by Rovibond®, which illustrates the difficulty the Japanese have in distinguishing between the L and the R.

mechanism, allows the claims to be formulated in such a way that they are far more difficult to circumvent than when they are based on observations alone. That does not imply that this insight has to be spelled out in the specification, far from it. After all, there should be a surprise element in the invention, and moreover, on the occasions where an explanation is given, the inventor does not want to be bound by it.

Coming back to Ibuki et al. (1993), I would not have applied for a patent at such an early stage of development. To me, the criteria by which the bleaching earth is characterized (specific surface area, silica content, and rust content) do not look as if they tell the whole story. According to Ruf et al. (2007), iron salts can activate bleaching clay, and so, yes, the iron content could well be an essential criterion. Adsorption needs a surface, and so, yes, surface area could be an essential criterion, but to me, introducing those criteria does not indicate any insight into what actually happens. That requires proper research and some inspiration.

Now we come to what is probably the most interesting development in bleaching processes over the last 20 years: the Öhmi countercurrent bleaching process, for which ten plants have been sold[19] so far. In the usual co-current bleaching process, spent bleaching earth is in equilibrium with bleached oil. This earth is capable of removing color from unbleached oil, which is what the Öhmi process aims to do. From a patent perspective, this process has a somewhat checkered history. There is the first priority document (DE 41 24 331 of 23 July 1991), which led to the European application (Transfeld 1993), which was withdrawn in 1995, and the US patent Transfeld (1994). There is a subsequent application (Transfeld and Börner 1993) that was only applied for and granted in Germany, and finally, there is the German priority document (DE 196 20 695 of 23 May 1996), which led to a European patent (Transfeld and Börner 1997), which is still in force in the designated states (BE DR GB NL and SE), and to the US equivalent (Transfeld et al. 1998). Not surprisingly, the Search Report of the latter European patent mentions US patent (Transfeld 1994). This European patent is characterized in that the bleaching earth that has been used once is obtained (isolated) as a pumpable sludge (slurry) while air is excluded. On paper, the Öhmi countercurrent bleaching process looks like a perfect solution to a long-standing problem, so the reason why more units have not been sold is far from obvious.

Another Öhmi development concerns the electrofiltration process. It makes use of the fact that small bleaching earth particles adsorb more (w/w) than large ones. Accordingly, using small particles can save on bleaching earth usage provided they can be removed from the oil. This removal is the object of an early application (Wetzel and Schneider 1996) that was not pursued and a later one (Börner et al. 1999) that was granted without the application having been published; it was not opposed but allowed to lapse. Finally, there is a family of process patents, including Transfeld et al. (2003), that are based on the German priority document (DE 197 11 174 of 18 May 1997). This led to a family of ten members, not counting the various European

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[19] G. Börner, Öhmi Engineering GmbH, personal communication.

countries that were designated in the European application. Like the previous patent, it was allowed to lapse. I do not know why it was allowed to lapse. There could be technical problems, a lack of market interest from refiners, or a boycott by bleaching earth producers. After all, if they refuse to supply bleaching earth fines, there is little point in maintaining a patent disclosing their use and removal.

Historically, fish oil has been hydrogenated to yield a hardstock for margarines and shortenings, and it was the hardstock that was bleached and deodorized. Nowadays, fish oil is used in fish feed and as nutritional supplement, and the oil itself has to be purified. Consequently, a number of patents and patent applications have been published on the subject of adsorptive cleaning of fish oil or marine oil in general. Tsujiwaki et al. (1998) disclose a process in which fish oil is alkali refined and bleached with normal bleaching earth, after which the bleached oil is contacted with diatomaceous earth that has been calcined after having been mixed with a flux (an alkali metal or alkaline earth metal salt or hydroxide).

In another application (Craven and Morrison 1999), a purification process for fish oil is disclosed that primarily aims to remove polychlorinated compounds and polycyclic aromatic hydrocarbons. It comprises adsorption by activated carbon and steam stripping. Its Search Report quotes two publications that are given an "X" with respect to the main claim and six documents with an "X" with respect to claims 7 and 14. Even so, the claims were not altered in the granted European patent (EP 1 084 214) or the granted US patent (6,469,187). This just shows that there is not necessarily any reason to panic when a Search Report is full of "Xs."

A subsequent patent application (Hjaltason 2002) also employs activated carbon to get rid of polychlorinated contaminants. Like the previous patent (Craven and Morrison 1999), it contacts the oil with this adsorbent under reduced pressure and in a similar temperature range of 30–95°C and then removes the adsorbent from the oil. It differs, though, in that Craven et al. refine and cold clear their oil, whereas Hjaltason characterizes his process by excluding prior steps of neutralization and/or winterization. Accordingly, a patent was granted in Europe (European Patent 1 303 580) in 2006, but in the US, failure to respond to an Office Action led to abandonment.

A Unilever application in the US (Misbah and Rosier 2008) also has a PCT equivalent. The Search Report of the latter refers to four documents, each of which has been given an X. The US application was abandoned and the European application is "deemed to be withdrawn." The process disclosed by Misbah and Rosier (2008) is concerned with "vulnerable oil," which (claim 3) turns out to be fish oil, marine oil, or microbial oil. It comprises at least one of four steps, whereby the bleaching step involves both a wet step and a dry step. Accordingly, a 50% solution of citric acid is added to the oil containing some bleaching earth, some water is added, and then the mixture is dried under vacuum.

Then filtration is conducted in a recirculation mode until the filtrate has a turbidity of 0.2 FTU or less, where FTU stands for "formazin turbidity units," an international standard that can be applied to any turbidity measurement. Introducing novel criteria is a well-known trick to emasculate prior art. This prior art may also have reported recirculation until the filtrate was quite clear, but if it did not quantify its clarity, this might have been outside the limits specified by this novel criterion. Accordingly, the introduction of this criterion means that potential prior art cannot be upheld. Sadly enough for the applicant, the trick did not work.

A further bleaching process for fish oils has been disclosed by Wang (2009), which led to US Patent No. 7,807,848[20] (5 October 2010). It prescribes heating the oil in the presence of bleaching earth to quite elevated temperatures (150–200°C) for quite extensive periods of at least 20 min (claim 3). This is likely to cause the double bonds in the fish oil to isomerize to their *trans* configuration, a reaction that obliterates some aspects of the supposed nutritional value of the fish oil. According to Arntsen (2010), marine and vegetable oils can be purified by adding a first absorbent selected from the group comprising[21] chitosan, carageenan (*sic*), collagene (*sic*), and alginates and then adding a second absorbent material, allowing the suspension to rest, and collecting the purified oil.

Nanomaterial can also be used to remove pigments from organismal oil. According to Vick et al. (2008), this nanomaterial should be carbonaceous (claim 13) and may comprise graphene (claim 26). The same nanomaterial can also be used to recover oil from an organism; subsequently, if the oil is recovered from the nanomaterial, this oil is substantially free from chlorophyll. I do not know what this nanomaterial costs, but the cost could well be prohibitive in the context of the biodiesel production envisaged. It might therefore make more sense to recover the nanomaterial from the oil. Moreover, current industrial processes to manufacture biodiesel from rapeseed oil do not include chlorophyll removal. Activated carbon can also be used in a column through which the oil percolates (Nakamura 2008) or be added as a powder to the oil and then removed by membrane filtration (Berge et al. 2010).

According to Van der Waal et al. (2009),[22] the efficacy of an antioxidant can be increased by bleaching the oil in two stages while adding the antioxidant (rosemary extract) in the first stage. Bleaching earth can be used in both bleaching stages, and activated carbon is preferably only used in the first stage. After bleaching, the (pine nut) oil has to be deodorized.

Several people have discovered that exchange resins can also be used to arrive at a light-colored oil. Lee and Pfalzgraf (2007) start by claiming, “A composition comprising a corn oil having a color value of less than 1.0 red on the Lovibond scale.” To me this raises the question of how to detect infringement since a composition with a color of, say, 0.9 R could consist of a mixture of a hardstock with $R > 1$ and corn oil with $R << 1$, which would infringe, but it could also consist of a hardstock

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[20] Just have a look at columns 17 and 18 in this patent. They just list ranges, such as, “from about 25 to 11, from about 24 to about 11, from about 23 to about 11, from about 22 to about 11,” and so forth, column after column. I would guess that mathematics could well offer a notation that would shorten these columns to just a single formula.

[21] Since the choice of adsorbent is limited to those listed.

[22] The company Lipid Nutrition B.V. is part of IOI Loders Croklaan, the IOI subsidiary that was formerly owned by Unilever.

with R<<1 and a corn oil with R>1, which would not infringe. In this respect, claim 8 makes more sense since it is concerned with the vegetable oil itself.

With respect to the process claims, the same duality can be noted in that process claim 12 refers to a composition, whereas independent process claim 28 refers to a miscella[23] of corn oil in a non-polar solvent. Both the composition and the miscella can be treated with a cationic ion-exchange resin and the resin can be regenerated with an acid. The treatment can entail suspending the resin in the oil or miscella or passing the oil or miscella through a column of resin beads. Another process claiming the use of ion-exchange resins has been disclosed by Banavali et al. (2009). It prepares oil as raw material for biodiesel production.

No patent review of bleaching processes would be complete without discussing contributions by Süd-Chemie. In 2009, Schurz disclosed a process in which he uses bleaching earth that has not been acid-activated and a preferably solid organic acid like citric acid to bleach oils and fats that have preferably been degummed to a residual phosphorus content of less than 15 ppm. In another application by the same inventor (Schurz 2010), a process is disclosed in which (palm) oil is water degummed and bleached with a preferably acid-activated bleaching earth before being deodorized. Not surprisingly, the Search Report lists two Oil-Dri patents (Brooks et al. 1991, 1992) that I will discuss in the next section.

7.4 Spent Earth Disposal

As mentioned in the general bleaching review (Study Group "Technologies for Industrial Processing of Fats and Oils," 2001), acid-activated bleaching earth can act as a catalyst and thereby cause spent earth to start to smolder and eventually auto-ignite. This tendency is especially pronounced when the oil in the spent earth is highly unsaturated. So it is not surprising that a bleaching earth that reduces spontaneous combustion has been promoted in the disclosure by Brooks et al. (1991). It is a neutral clay comprising attapulgite and smectite within specified ratios that contains a chelating polycarboxylic acid with an even number of carboxyl groups. No arguments or comparative experiments are provided that rule out polycarboxylic acids with an odd number of carboxyl groups, so I would guess that specifying an even number is a means of avoiding prior art (citric acid). As not unusual in the US, the application was split into a process patent (Brooks et al. 1991) and a product patent as continuation in part (Brooks et al. 1992). The abstracts, figures, and specifications of the two patents are identical, and only the claims differ. In another process (Flessner et al. 1997), the catalytic activity of the acid-activated bleaching

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[23] It calls this solution a "composition comprising corn oil and a non-polar solvent," but the fact that it yields corn oil on solvent evaporation shows that it is a corn oil miscella. So the word "comprising," which normally means that further compounds besides those listed may be present should be read as "consisting of," which limits the mixture to those compounds that have been listed.

earth is reduced by neutralization. The spent earth is sprayed with an aqueous solution of an alkaline compound such as lime, caustic, or soda ash.

These patents illustrate the fact that spent bleaching earth can present a problem. Vertically integrated plants that comprise an oil mill and a refinery have less of a problem since they can mix the spent earth with crude oil and pump the resulting slurry to the oil mill, where the oil is extracted from the spent earth and the extracted earth forms part of the meal. The problem arises in stand-alone refineries where solutions outside these refineries are needed (Chung and Eidman 1997; Zschau 1994). Solutions for use within these refineries that have been investigated include deoiling with supercritical carbon dioxide (Waldmann and Eggers 1991, 1992). This process also aimed at regenerating the bleaching earth, but the extraction residue had only half the activity of the virgin earth. The use of a supercritical fluid, preferably carbon dioxide, is also disclosed in a patent application (Saebo 2009). This application includes an apparatus claim that specifies that the same vessel that is used to bleach the oil is also used to deoil the spent adsorbent. This must make the bleacher very expensive, but then the pharmaceutical nature of the application reveals that we are talking about products that can stand this kind of expense.

In another regeneration process (Nebergall et al. 1994), most of the entrained oil is removed with water, and then the earth that still contains some oil and chlorophyll is oxidized, for instance, with hydrogen peroxide, and finally, the cleaned earth is acid-activated to restore its bleaching activity. Schmutzler and Trujillo-Quijano (1994) claim that they can regenerate granular spent bleaching earth that has been used to bleach a hexane miscella by extracting the granules with a hexane/polar solvent mixture. They mention anhydrous ethanol and acetone as polar solvents but do not illustrate their effectiveness in an example.

A problem with these and other extraction processes (Camp 1997; Lee et al. 2000; Nakaoka et al. 2003; Rothbart 1997; Santos 1999) is that the oil in the spent earth is prone to react and polymerize so that not all the oil can be extracted. Similarly, a transesterification of the oil that is retained in the earth with an alcohol (Kaimal et al. 2003) to form fatty acid alkyl esters will not cause all organics to be removed. The extractable oil content of cakes can be quite a bit less than the weight loss on ashing (Morton 1995). Accordingly, the oil loss on bleaching should not be based on the amount of oil that can be extracted from the spent earth but on the weight loss when spent earth is put in a muffle furnace (Dijkstra 2007b). Using this method reveals that spent bleaching earth, even when it has been blown with steam or nitrogen, contains at least 35% organics by weight. Accordingly, its fuel value is comparable to that of lignite, and that poses temperature-control problems on removal by burning.

Such problems were faced when the regeneration of synthetic bleaching compounds was developed (Lammers and Groeneweg 1990; Staal et al. 1990). Their regeneration process was presented in more detail by Kuin and Nock (1992). It comprises a first calciner in which the spent adsorbent containing some 35% oil is heated in an inert (nitrogen) atmosphere. In a second calciner, the residual oil is burned off under air atmosphere. The reason for this two-stage treatment is that burning off all the oil in the spent adsorbent would raise the adsorbent temperature above the upper limit and cause the pore structure of the adsorbent to collapse. However, two-stage oil removal is expensive, so Maes and I (1993) subsequently disclosed a single-stage process in which the heat of combustion is dissipated in a fluidized bed of sand particles that is so tall that all organics have been burned off by the time the clay particle is blown out of the fluidized bed.

We felt that developing this process on an industrial scale was somewhat outside the scope of our employer, so we proposed a joint development and exploitation to Süd-Chemie. This company was quite interested since, as it turned out later, it was working on the regeneration of spent earth itself. Like us, it knew that uncontrolled combustion would lead to unduly high temperatures that would cause the pore structure of the earth to collapse. So in their first patent application (Hähn et al. 1995), they reduced the oil content of the spent earth by solvent extraction, but this application was soon withdrawn. In a second patent application (Ebert et al. 1997), they tried to circumvent our Vandemoortele process by mounting a heat exchanger above the fluidized sand bed. A patent was granted and maintained until 2010.

None of these regeneration patents has been exploited industrially for the bureaucratic reason that spent bleaching earth is regarded as a waste product. Burning waste may lead to dioxin formation, and to prevent this dioxin[24] from being released into the atmosphere, the gases have to be heated in the presence of air to such a high temperature that the clay particles partially melt and lose all bleaching activity.

7.5 Removing Cholesterol from Oils

The patent literature reveals an astounding awareness of what subjects are suddenly fashionable. One company is working on a subject, its application is published, and lo and behold, shortly afterwards, several other companies apply for patents in the same field. The first time I became aware of this contagious nature of research subjects was when I was still working for ICI. It was also the reason I switched from gas kinetics to material science.

I was working for ICI, in a British research laboratory, when AKU[25] applied for patents claiming an injection molding process for polyethylene terephthalate (PET). They even had a trademark: Arnite®.[26] AKU had applied in the Netherlands, and so the published applications were in Dutch. In this research laboratory, I was the only person who understood Dutch, so I was asked to translate all these applications as a matter of urgency. After I had done that, I was quite familiar with the subject and decided to continue working in this field. This led to my first patent (Dijkstra et al. 1967).

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[24] The fact that dioxin is far less toxic to man than to rats is immaterial in this context.

[25] This is the Algemene Kunstzijde Unie, Arnhem, the Netherlands, which merged in 1969 with Koninklijke Zout Organon to form AKZO. In 1994, this company acquired Nobel Industries, Sweden, and became Akzo Nobel.

[26] This is now produced and marketed by DSM Engineering Plastics, and the trademark is even used for Nylon 6 and PBT engineering plastics.

When I subsequently worked for ICI in their polyester polymer plant in the Netherlands, I had a number of PET balls made and placed them in the rotary sieves underneath the dicers. The ball rubbed against the polymer granules and detached their threads[27] so that these could be removed. If these were not removed, the polymer would segregate on transport to West Germany and cause problems in the spinning plant. Because the balls were made of PET, this prevented the granules from being contaminated with another polymer.

A more recent example of research being contagious is biodiesel. FAME were known for a long time and used in the oleochemical industry as an intermediate in the production of fatty alcohols. However, when biodiesel became fashionable, a sudden flutter of patents dealing with biodiesel emerged. On a smaller scale, the removal of cholesterol from edible oils has also been a fashionable subject. This is illustrated by the spate of applications that I will discuss below. They nearly all date from the early 1990s, and the last publication dates from 2004. Since most removal processes operate by adsorption and only a few by stripping, the place to discuss them is at the end of the bleaching chapter and just before the deodorization chapter.

I get the impression that the interest in cholesterol removal started within the dairy industry since dairy companies applied for and also opposed patents. Interest from these quarters can be explained by the fact that milk fat is expensive and can presumably stand the cost of some additional treatment. Moreover, claiming "with reduced cholesterol" or even "without cholesterol" might strike some people as a strong marketing argument.

The Search Report of an application (Keen 1989) made by the New Zealand Dairy Research Institute quotes an earlier application by the same institute, and a patent granted to Monserbio,[28] France (Bayol et al. 1989) was opposed by the Australian CSIRO and the Belgian milk fat company Corman. This patent employed cyclodextrin as cholesterol adsorbent, so a manufacturer of this adsorbent, SKW Trostberg, Germany, also opposed. As a result, the patent had to be amended. This patent also had a follow-up (Courregelongue 1992) disclosing how to regenerate the cyclodextrin with a lower primary alcohol. While the patent was still under examination, its rights were transferred to another company (Asterol), and then it was withdrawn. In yet another Monserbio patent (Montet et al. 1990), the oil is extracted with brine containing a biliary salt and partial glycerides of unsaturated fatty acids; the extraction may have to be carried out several times. Example 2 uses 1 g of AMF (anhydrous milk fat) and 60 g of the brine solution, which must make it an expensive process; even so, only 40% of the cholesterol present in the AMF is extracted.

Corman (Roderbourg et al. 1990) also used an O/W emulsion whereby the water contains 3–8% of a cyclodextrin, preferably β-cyclodextrin. The water is finely dispersed and subsequently separated by centrifuge. Cyclodextrins are also used in the

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[27] In Dutch, these are called *hakbaarden* ("chopping beards"). I learned this word from a friend who worked in an AKU spinning plant.

[28] I tried to find out more about this company through a Google search but was only referred to its patents.

processes disclosed by Roquette Frères, a French starch company manufacturing cyclodextrins. These were used at CIRAD in Montpellier, and this work led to a patent family of 16 members, including (Graille et al. 1993). These patents disclose a process to remove cholesterol from dairy products by mixing cream with cyclodextrin before churning. This causes cholesterol to combine with the cyclodextrin and be removed with the buttermilk.

Work at Roquette Frères continued and on 29 January[29] 1990, this company filed four applications with the French Patent Office, which were assigned the numbers 90 01007–90 01010. The first of these applications also led to a European application (Mentink and Serpelloni 1991b) and a patent that was opposed by Wacker Chemie, Germany, as a result of which the patent was revoked in September 2000. Roquette Frères, foreseeing this outcome (?), stopped paying annuities and allowed the patent to lapse in 1998. The patent discloses a treatment with cyclodextrin that leads to complexes that do not contain free fatty acids. It also prescribes a thermal treatment that is preferably carried out in two stages.

The second of these applications (Mentink and Serpelloni 1991a) is concerned with complexes that do contain free fatty acids. The granted patent was not opposed but nevertheless allowed to lapse in 1998. The third application (Comini and Mentink 1991) discloses a process in which the cyclodextrin complexes are washed with an anhydrous polar solvent that causes these complexes to dissociate. The granted patent was not opposed but also allowed to lapse in 1998. The fourth application never got any further than a French application that was granted but allowed to lapse by non-payment of annuities. It discloses an acid and/or enzymatic hydrolysis to degrade the cyclodextrin complex. Apparently, little or no cyclodextrin was sold for cholesterol removal, so maintaining the patents by paying the annuities was considered to be an unnecessary expense.

The University of California studied saponin as a means to remove cholesterol from dairy products, and as it turned out, they filed a first application in 1989. I became aware of this research through (Richardson and Jiménez-Flores 1991) and (Sundfeld and Richardson 1994), two PCT applications with the same flow diagram on the bibliography page. This diagram shows that the dairy product is first mixed with saponin and then with a filter aid, after which the mixture is separated. This yields a liquid product containing the cholesterol-reduced dairy product and a solid product that can then be separated into its constituents: saponin, cholesterol, and filter aid. These applications have a somewhat checkered history.

The first thing that struck me as odd was that their claims were almost identical even though the earlier application uses numbers, whereas the later one uses letters (AA, BB, CC, etc.). There were also differences in inventors, title, and length (44 pages for the earlier one and 65 pages for the later one). Looking at the INPADOC patent families showed these to be identical by listing the same seven publications, which included two granted US patents. Consulting the Patent Application Information Retrieval (PAIR) at the USPTO website revealed that a first US

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[29] This happens to be my wife's birthday.

application (07/421,153) had been filed on 13 October 1989. This application forms the basis for the earlier PCT application. In the US, this application was abandoned and continued on 15 October 1990 as application 07/598,356. This was also abandoned and continued as application 07/906,108, which led to US Patent No. 5,326,579. This application was further continued on 24 November 1992 as application 07/980,981, which led to US Patent No. 5,370,890 and which also forms the basis for the later PCT application in 1994. The Australian, Canadian, and Japanese applications are all based on the earliest US application (07/421,153). Things can get rather complicated.

Through one of its affiliate companies, SKW Trostberg was a producer of cyclodextrin. So it is not surprising that it joined the cholesterol removal bandwagon. In Heidlas (1994), a process is disclosed that uses nozzles to mix the fat containing the cholesterol with the aqueous solution of cyclodextrin. This application did not lead to a patent since it was withdrawn in 1998. Instead of nozzles, a mixing device or in-line mixer can also be used (Ritter et al. 1996). Another SKW application (Cully et al. 1992) discloses how to remove residual cyclodextrin from oil with a microbial amylase. It led to a granted patent that was allowed to lapse by non-payment of the annuities. That also holds for the priority document (DE 43 13 919) of the US patent, Kohlrausch et al. (1996), which discloses how to use cyclodextrin to remove cholesterol from eggs. However, like other patents disclosing ways to remove cholesterol from eggs (Klemann and Finley 1991; Massie 1993), this application is outside the scope of this work.

Now we come to two US patents, both of which "disclose" that treating an oil with a cyclic anhydride such as succinic anhydride causes this anhydride to react with the hydroxyl group of cholesterol to form a cholesteryl hemisuccinate. This compound has a free carboxyl group, which means that it can be washed out of the oil with alkali. Instead of succinic acid, glutaric acid can also be used. The reaction is like the reaction with acetic acid anhydride used to determine the hydroxyl value of an oil.

The intriguing thing about these patents is that the patent with the earlier application date (Wrezel et al. 1992) was granted on 7 July 1992, which is after the filing date of 9 November 1991 of the second patent (Hammond and Chen 1993). Consequently, the early patent cannot be regarded as prior art for the later one. So the USPTO should grant the early applicants what they claim and grant the later ones what would be left of their claims. However, in the US, patent rights go to "the first to find" rather than to "the first to file," so if Hammond and Chen could prove that they made their invention before Wrezel et al. (or could demonstrate that they knew it by the time Wrezel et al. made their invention), they should be granted what they asked for (and leave Wrezel et al. with the leftovers). So I tried to consult the file wrapper on this, but sadly enough, correspondence from the early 1990s is not accessible from behind my desk. It is a pity, because it would have been most interesting.

Another patent involving a chemical reaction (Roczniak et al. 1991) is based on the observation that adding calcium bromide to an oil containing some cholesterol causes a precipitate to be formed consisting of a complex between this salt and cholesterol. This can be removed by filtration or centrifugation, and the oil can be washed with water to remove the excess salt and dried. Contacting an oil containing cholesterol with charcoal that has been activated in a special way is claimed to remove cholesterol (Athnasios and Templeman 1992). The process also claims to remove saturated fatty acids, but how it can do so when it "does not remove a substantial portion of any unsaturated fatty acids which may be present in the mixture" is not clear to me. The examples show this removal of stearic acid to be small. Although the main claim does not mention that the oil is treated as a miscella, all examples use various solvents.

According to Awad and Gray (2000), the neutralization process can be combined with cholesterol removal by first converting the FFA with an alkali metal base into soluble soaps and then converting these soluble soaps with an alkaline earth metal salt[30] into insoluble soaps that are then removed from the oil. If this is done in the presence of a cyclodextrin, cholesterol is removed at the same time. A certain affinity of cholesterol for phospholipid bilayers has also been reported (Kodali 1999). Mixing lecithin with water and dispersing the mixture in an oil containing cholesterol and subsequently separating the oil from the aqueous phase reduces the cholesterol content of the oil. However, to be worthwhile, the treatment has to be repeated several times. Increasing the ratio of the lecithin to the oil also increases the proportion of cholesterol removed. A totally different approach was disclosed by Bijl[31] et al. (2000). They wash the oil with ethanol containing up to 5% water. This removes polar compounds such as partial glycerides and also some sterols. The process has been developed especially for the purification of microbial oils.

In 1990, Hoche[32] applied for a European patent disclosing a process, product, and equipment to remove cholesterol from anhydrous milk fat by vacuum steam stripping. It was granted and the family list consists of 21 members[33] that were maintained until 2007/2008. The equipment used is not remarkable in that it employs a horizontal tubular deodorizer as already disclosed by Lau in 1965. Chang et al. (1989) disclose a process to purify fish oil that starts with deodorization at a fairly low temperature (<15°C) and continues with a silica adsorption treatment. Accordingly, this process not only reduces the cholesterol content of the oil, but it also removes other undesirable constituents selected from the group consisting of polymers, pigments, pesticides, PCBs, heavy metals, and mixtures thereof.

A short path distillation was disclosed by Johnson and Conte (1991) to provide a low-cholesterol animal fat product. An entrainment aid such as monoglycerides and even digycerides is mixed with the fat to be purified. Massie et al. (1995) disclosed a thin-film countercurrent vacuum stripping process for animal fats like butter oil and chicken fat. In the same patent, they also disclose a process in which egg yolks are mixed with deodorized (i.e., reduced in cholesterol content) oil and

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[30] The Abstract refers to these salts as "alkali metal salts"; the claim does not make the same mistake.

[31] Bijl is an inventor who is regularly cited in Chap. 2, in the section dealing with single-cell oils.

[32] The patent was later assigned to Hoche Butter GmbH.

[33] The US equivalent is 5,340,602.

the mixture is separated into a defatted egg yolk fraction and an oil phase that can then be deodorized to reduce its cholesterol content. What struck me in this patent is that the Abstract only describes the second process, whereas the detailed description does not describe this second process at all; that is only shown in the examples. In a subsequent application, Massie (2004) discloses a special thin-film deodorizer in which the steam flow drives the oil upward on the support surface as a rising turbulent film; the application never made it to a patent because it was abandoned.

Finally, I want to discuss an application (Sondbø and Thorstad 2004) that shows that media other than steam or nitrogen can be used in vacuum stripping. It specifies the use of a "volatile working fluid" having more or less the same volatility as cholesterol. Said fluid comprises a fatty acid ester, a fatty acid amide, or a hydrocarbon. Since these compounds have a higher relative molecular mass than steam, their amount has to be increased, but by using molecular distillation or short path distillation, the very low vacuum in these installations causes the amount to be decreased again. The application by Sondbø and Thorstad (2004) is part of a 30-member family.

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Chapter 8
Dewaxing

8.1 State of the Art in 1990

In Europe, the removal of wax from oils such as sunflower seed oil or corn germ oil is commonly referred to as “winterization.” However, when I used this term in the US, people thought I was referring to a process to remove higher-melting triglycerides from an oil such as cottonseed oil or brush hydrogenated soybean oil, a process that is called “dry fractionation” in Europe. So to avoid any ambiguity, I will talk about dewaxing and dry fractionation and avoid the use of the term “winterization.”

Waxes are esters of fatty acids and fatty alcohols, and just as with triglycerides, their melting point goes up as the fatty acid chain increases in length and goes down with chain desaturation. Sunflower seed waxes have a low unsaturation level, so they have a high melting point and a low solubility at refrigerator temperatures. So if non-dewaxed oil is stored in a fridge, it will develop an unsightly deposit of wax crystals; if this oil is used to make mayonnaise, these crystals will destabilize the emulsion. So for salad oil and mayonnaise, oil has to be dewaxed, but this is not mandatory for oil to be used in margarine or shortening.

The low solubility of wax in oil at low temperatures, where the oil remains liquid, forms the basis of common dewaxing processes. They cause the wax to crystallize by cooling the oil, and then they remove the crystals. There is a problem, though. The oil viscosity increases considerably when the oil is cooled down. This causes oil to pass more slowly through a filter and also decreases the capacity of centrifugal separators.

At what stage of refining the oil is dewaxed is not critical.[1] Certain degumming processes (e.g., Ringers and Segers 1977) comprise a cooling stage that causes some of the wax present to crystallize so that on subsequent gum removal by centrifugation,

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[1] This is an expression that is often used in patent specifications. It aims to widen the field in which the invention can be profitably applied and thereby to increase the scope of protection.

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at least some wax is removed. This removal tends to be incomplete so that "cold degumming" requires a second dewaxing treatment by filtration since that is the only wax removal treatment that ensures that the dewaxed oil has good cold stability. Wax removal by the use of soap in a kind of detergent fractionation (Gonçalves Antunes et al. 1984) also tends to be incomplete. Since the amount of filter aid used and the loss of oil in the filter cake lead are proportional to the amount of wax that is removed, Denise (1987) recommends to pre-dewax oils with a wax content above 600 ppm by centrifugal separation and then remove the residual wax by filtration.

On the other hand, treating crude or water degummed sunflower seed oil with >800 ppm of wax with an aqueous solution of EDTA, cooling to 7°C, and holding it at that temperature for 8 h before separating the gums and wax by centrifuge also led to an acceptable cold stability without filtration (Tirtiaux and Gibon 2001). Since deodorization is usually the last step in oil refining, dewaxing tends to precede deodorization but not necessarily. Dewaxing can also be combined with bleaching and thus save on a filtration step (Anghelescu et al. 1986).[2] Some people consider the dewaxing process to be a sure means of eliminating any solid triglycerides that might have originated from cross-contamination during deodorization.

In the case of physical refining, the oil being deodorized still contains free fatty acids. So when I worked on the development of the Total Degumming Process (1989), I also investigated if totally degummed oil could be dewaxed. It was found[3] that for the same wax content, the cloud point of totally degummed oil was slightly lower than for neutralized oil but that otherwise, the behavior of both oils was identical.

During the dewaxing process, the oil is cooled to cause the wax to crystallize, which it starts to do when the cloud point of the oil is reached. Good filtration characteristics, such as a low filter aid requirement, slow pressure buildup, and low oil retention in the filter cake, result from large wax crystals, and so care should be taken to generate such large crystals. In practice, avoiding the formation of many small crystals means that once nuclei have appeared, they should be allowed to grow without many further nuclei being formed. This necessitates well-defined temperature control once crystallization has started, *ergo* at the cloud point.

This cloud point depends on the amount of wax present, which therefore should be determined on a regular basis. In sunflower seed, the wax coats the hull. Accordingly, dehulling the seed prior to oil extraction leads to an oil with a lower wax content than extracting oil from non-dehulled seeds. In addition, the wax content also depends on the cultivar.

As has been exposed before (Dijkstra 2007), the literature provides widely diverging views on how to avoid further formation of nuclei once some nuclei and crystals have appeared. Some people cool fast and store the cold oil for several hours in maturation vessels (De Greyt and Kellens 2000; O'Brien 2000). They claim that this maturation leads to larger crystals by an Ostwald ripening process, but the

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[2] In the US, the equivalent patent (No. 4,981,620) was not granted until 01.01.91.

[3] This is a personal communication from J. De Kock, who also optimized the winterization cooling profile.

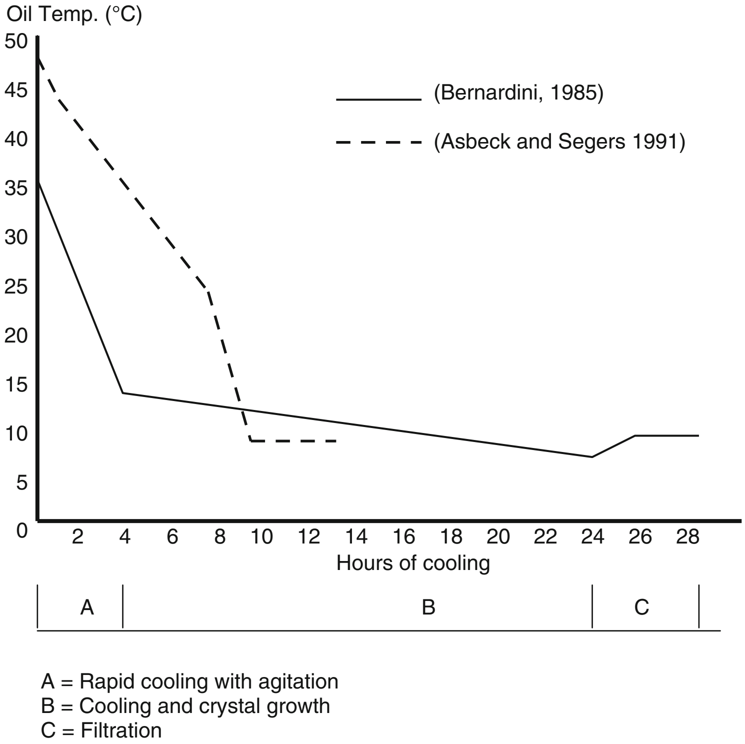

Fig. 8.1 Cooling profiles during dewaxing. Adapted from Inturrisi (2007). *A* Rapid cooling with agitation, *B* Cooling and crystal growth, *C* Filtration

literature provides no experimental proof of this claim. The solid line in Fig. 8.1 illustrates the resulting temperature profile.

Asbeck and Segers (1991), on the other hand, advocate

> a first cooling step in which the oil is quickly cooled to the solubility temperature of the wax present in the oil (about 45°C) and a second cooling step comprising a cooling rate of 6°C per hour and a maximum temperature difference between the oil and the coolant medium of 8°C. The oil end temperature was 8°C. The oil/crystallized wax slurry obtained was immediately microfiltered without any additional maturation time.

Their temperature profile is represented by the dotted line in Fig. 8.1.

8.2 Developments Since 1990

Apart from advocating a temperature-control system that leads to large and reasonably uniform wax crystals, Asbeck and Segers (1991) also avoid the use of a filter aid by employing a microfilter. They limit themselves to oil with a water content of less than 0.5% and demonstrate that this has advantages. Their examples show that the filtrate (dewaxed oil) remained brilliant after the cold test, but they do not report the oil content of the concentrated waxy retentate. The Search Report of this patent mentions the German equivalent of Mutoh et al. (1985) that discloses filtration by means of a porous membrane, which is not only useful “for dewaxing a vegetable oil but also for removing a wax together with a phospholipid, a free fatty acid and water from a crude vegetable oil.” That is presumably the reason why (Asbeck and Segers 1991) is limited to dry oil.

This patent is cited as a reference in Muralidhara et al. (1996),[4] whose “invention provides for the separation of higher melting glycerides (*sic*) from vegetable oils.” The reason for this quotation is not so much the rate of cooling, since Muralidhara et al. specify a cooling rate of 40–1,650°C per hour, but the use of a porous, non-metallic inorganic filter. Like the prior art, they do not mention the oil content of the retentate either, only the absence of a filter aid.

Dewaxing sunflower seed oil by the detergent process leads to an aqueous effluent stream that contains wax and some oil. Purtle et al. (2006) are concerned about this effluent and want to recuperate its organic constituents. Accordingly, they acidify the aqueous effluent and extract it with an organic solvent such as hexane. When the hexane is cooled, the wax crystallizes so that it can be recuperated as such while leaving a miscella from which the oil can be recuperated. The Search Report of this application lists ten documents, each of which has an X. Even so, a request for examination was filed with the EPO and further fees were paid, but eventually, when no reply was received to an examination report, the application was deemed to be withdrawn.

Tokarev & son,[5] on the other hand, obtained a patent in 2009 following their application in 2007. They regenerated the filter aid used during wax removal by filtration by mixing oil into this cake and heating the mixture until all the wax has melted. Subsequent centrifugation yields a filter aid with reduced wax content that can be re-used and oil containing wax. It “is sent to the warehouse for selling to third parties as a new grade product.”

A process to dewax oils by the distillative removal of the fatty alcohols that have been obtained by hydrolysis of the wax molecules was disclosed by Bada Gancedo et al. (2007). Reformation of the wax esters must be prevented by avoiding reflux of the components to be distilled.[6] Finally, I want to discuss an application by W.R. Grace & Co. (Jalalpoor 2009). It discloses the addition of a liquid nucleating agent such as, for example, colloidal silica, alumina, zirconia, or

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[4] In this patent, the USPTO refers to this former vice president of Cargill as “Muraldihara.” So I went to the USPTO website and carried out a quick search with IN(ventor) Muraldihara AND AN (assignee name) Cargill: 3 hits. Then I spelled his name correctly IN Muralidhara AND AN Cargill: 13 hits.

[5] The first inventor is called Tokarev, Vladimir Dmitrievich, and since the second inventor is also called Tokarev and his patronymic is Vladimirovich, I assume him to be a son of the first inventor.

[6] The application itself is in Spanish, but it contains an English abstract. A patent has only been granted in Spain.

titania, or mixtures thereof in water, to the oil to be dewaxed. According to the examples, the oils processed according to the invention had a better cold stability than the oils that had been dewaxed in the absence of these colloidal metal oxides. This indicates that they can have an effect, but it does not demonstrate that the same effect cannot be attained without them. Perhaps they cause the crystallization to start earlier, and perhaps the cooling profile used was such that an early start of crystallization favored a good cold stability. The fact that there are processes that arrive at an oil with good cold stability without using these colloidal nucleating agents shows that these agents are not essential and that the application should be regarded as publicity, a sales brochure.

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Chapter 9
Vacuum Stripping

9.1 State of the Art in 1990

Before discussing the deodorization and physical refining processes in detail, I want to devote a few words to a common misconception that describes them as a "steam distillation." Steam distillation processes are used to purify organic compounds that are immiscible with water. During steam distillation, there are three separate phases (*P*): the liquid organic phase, liquid water, and vapor. There are two components (*C*): the organic compound and water. Thus, according to Gibbs' phase rule, the number (*F*) of degrees of freedom equals

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

This single degree of freedom means that either the system pressure or the temperature of the system can be chosen freely, but not both; the one determines the other. During stripping processes, on the other hand, there is only a single liquid phase besides the gaseous phase ($P=2$), so that the number of degrees of freedom increases to 2. Consequently, both the pressure and the temperature can be chosen without the value of the one determining the value of the other. Accordingly, there is a fundamental difference between a steam distillation process ($C=2$; $P=3$; $F=1$) and a vacuum stripping process ($C=2$; $P=2$; $F=2$). In addition, there is also the flashing process in which oil containing some FFA is exposed to vacuum ($C=2$; $P=2$; $F=2$). Here the number of degrees of freedom equals 2, which means that at a given temperature, the pressure can be chosen, but then, it determines the residual FFA content of the oil.

I appreciate that some readers will consider this introduction to be superfluous and perhaps even regard it as an affront to their intelligence, but allow me to invite them to have a look at Sampalis and Massrieh (2009) and see for themselves how confused some authors can be. All the process claims in this application end with a step that prescribes "**distilling under vacuum** the marine oil of step …." When I look at the specification, I read: "[0077] … The samples were filtered through a

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filter paper and subjected to **thin film vacuum steam distillation** using 95% ethanol and water." To me this looks like stripping, which is not the same as a vacuum distillation. Similarly, the DSM application Keller et al. (2008) claims, "A process for the preparation of a deodorized and stabilized food-grade marine oil which process comprises submitting a marine oil to a **counter-current steam distillation** (CCSD) in a thin film column containing a structured packing and, if desired, adding antioxidant(s)." They obviously mean a vacuum stripping process.

The early vacuum stripping processes aimed at deodorization. They were batch processes and they had the advantage of avoiding cross-contamination when changing to a different oil composition. Moreover, the entire batch had the same thermal treatment. However, their thermal efficiency was poor (Dijkstra 2007). Gradually, improvements were introduced, and by 1990, most batch processes had been replaced by continuous or semicontinuous deodorization processes, which have the advantage that they allow heat to be exchanged. Accordingly, they comprised heat exchange trays that were stacked one above the other and thereby grew into massive towers. Of course, continuous deodorizers had been known from the literature for a long time (Bollmann 1925), but as shown by Andersen (1962), early continuous deodorizers using countercurrent flow through bubble caps had the disadvantage of a decreasing vacuum from top to bottom. This was overcome by the cross-flow system in which each tray is directly connected to the vacuum system. According to Bernardini (1993), equipment comprising packed columns with a countercurrent movement of the stripping medium was used for the physical refining of palm oil in Malaysia at the time of writing.

I have had the privilege to visit an early continuous deodorization plant in Dieppe,[1] France. It operated a Raffaetà deodorizer in which oil trickles down an annular container that is filled with packing material. The container has perforated walls, and steam that is introduced into the annular space between the vessel wall and the container flows transversely through holes in the container walls to the vacuum system. According to the patent (Raffaetà 1959), oil leaving the annular container at the bottom can be recirculated, but I do not remember if the Dieppe plant did so. Accordingly, the Raffaetà deodorizer operated according to the same cross-flow principle as the tray deodorizers mentioned above.

9.2 Subsequent Developments

Semicontinuous deodorizers require trays with valves that are shut when the tray is filled from above and while the tray contents are heated, deodorized, and cooled. A way to make the trays self-draining was disclosed by Cook and Sewell (1995). The same

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[1] At that time, the plant in Dieppe was owned by my former employer Vandemoortele, but now it is owned by Saipol, a 100% subsidiary of Soprol, the oilseed division of Sofiprotéol. I do not know if the Raffaetà deodorizer is still in operation.

inventors also disclosed a vessel to be used in the removal of fatty acids from oil by vacuum stripping (Cook and Sewell 2001).[2] It allows the oil to be heated while the stripping medium not only provides the agitation required for heat transfer but also the volatilization of FFA. This combined action enables the treatment to take place at reduced temperature, which avoids *trans* isomer formation and carotene retention when palm oil is deacidified. A continuous stripping vessel was disclosed by Taylor (1999). It operates by the oil being sprayed (atomized) with the resulting oil droplets falling through a stream of stripping medium. A flash vessel was disclosed in (Albers and Schardt 2009). The oil containing FFA is spread over the inside of the vessel wall and volatiles are condensed on a central condenser, where they are contacted with a liquid into which the condensate dissolves. This dissolution decreases the vapor pressure of the volatiles and thus increases the driving force for the transfer of the volatiles toward the liquid. Without this liquid, the vapor pressure of the condensate might limit the evaporation of the volatiles from the oil.

A similar short- path distillation process was disclosed by Topitsch (2009). He also notes the above limitation and therefore introduces a vapor into the distillation vessel that condenses on the central condenser and dilutes the condensate originating from the oil to be purified. According to the inventor, causing the diluent to condense is more effective than supplying it as a liquid, as disclosed in Albers and Schardt (2009).[3] The diluent is selected from the group of fatty acids, fatty acid methyl esters, glycerol, and their mixtures. The vessel wall is kept at a temperature of preferably some 170–210°C and the condenser at preferably 15–40°C, while the pressure is preferably maintained somewhere between 0.005 and 0.015 mbar.

In vacuum stripping systems using steam as the stripping medium, the stripping steam, the motive ejector steam, and the organic vapors have to be condensed. Originally, this was done by spraying the vapors with water, but later deodorizers also included vapor scrubbers. Their importance increased when physical refining was introduced since this increased the amount of distillate. At the end of the 1980s, the dry condensing system, in which the vapors leaving the deodorizer are frozen onto one of two parallel surface condensers, had not yet been introduced although it had already been disclosed (Merk 1989).

In the dry condensing process, two condensers are used so that while one is being filled with condensate, the other can be cleaned by melting and draining what had been deposited on its surface. Since the low-temperature condensation only leaves non-condensable gases, they can be compressed by mechanical pumps. Consequently, the aqueous effluent of the dry condensing system is limited to the stripping steam, and steam consumption is much reduced. On the other hand, the electrical energy requirements and the investment are higher, so the optimal choice of condensing system depends on local circumstances. In general, large installations tend to profit from the dry condensing system.

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[2] I found it interesting to note that the later patent contains a figure that also appeared in the earlier one. Let's save some money by recycling.

[3] I would think that mixing the oil to be purified with liquid diluent would be even more effective.

In the US, this patent (Merk 1989) was applied for and assigned to the engineering company Atlas Danmark A/S. However, the rights to the Australian, European, Japanese, and South African applications were transferred to Unilever. In Europe, a patent was granted and no opposition was filed, but even so, it was allowed to lapse at around the time when Unilever sold nearly all its oil mills and most of its refineries. A subsequent development of dry condensing was disclosed by Jellema and Nijdam (2003).

Whereas the dry condensing system reduces the amount of gas that has to be evacuated from the scrubbed vapor to the non-condensables that were present in the oil and leaked into the apparatus, several inventors (Huesa Lope and Dobarganes García 1991; Cheng et al. 1992; Krishnamurthy et al. 1992) increased this amount by using nitrogen as stripping medium. The Krishnamurthy patent is a continuation of an abandoned application that was also a continuation of an abandoned application that had a priority date of 13.02.84. Accordingly, the other two patents have not been quoted as prior art, but the Spanish one (Huesa Lope and Dobarganes García) has been quoted as prior art in US Patent 5,241,092, the equivalent of Cheng et al. (1992), which was continued in part and led to US Patent 5,374,751.

Table III in the Spanish patent lists higher diglyceride and FFA contents for the oils that have been stripped using steam than for those stripped with nitrogen. Accordingly, the inventors conclude that deodorization with steam leads to hydrolysis of the oil. Moreover, they also observe a lower content of oxidized and dimerized triglycerides in the nitrogen-treated oils than in the steam-treated oils. From an oil-quality viewpoint, nitrogen seems to have advantages. A request for examination was filed, but the application was deemed to be withdrawn in 1994, but it is anyone's guess why file 90112499 at the European Patent Office has been destroyed.

The main claim of Cheng et al. (1992) prescribes the use of a non-condensable stripping medium and stipulates that the "amount of said non-condensable inert gas introduced or injected is substantially less than the theoretically required amount for deodorizing said edible oil and/or fat." Fortunately, this rather cryptic expression is explained in the summary of the invention. It "means an amount of non-condensable gas, which is sufficiently less than the theoretically required amount so that the cost of using non-condensable stripping gas is equal to or cheaper than using steam stripping gas." Sounds great, but I still do not understand what it means and it also raises a legal question.

Say I want to reduce the FFA content of an oil to 0.05%. I use the well-known Bailey equation (Bailey 1941), fill in values for the variables in this equation, and arrive at a theoretical stripping medium consumption in moles of medium per mole of oil. In accordance with the teaching of the patent, I use less stripping medium, as a result of which the FFA content of the deodorized oil is more than 0.05%. In fact, the FFA content is in accordance with theoretical results, so it is impossible to infringe this patent!

And what about when a theory evolves? How will this affect infringement? Just imagine that you operate a process in which you do not use less inert stripping medium than theoretically required and a new theory is put forward claiming that you use less than the original theoretic requirement after all. When reviewing the *Physical aspects of vacuum stripping* in general and the *Fatty acid vapor pressure* in particular (Sect. 3.9.1.2 in Dijkstra 2007), I explained the physicochemical background of positive deviations from Raoult's law. When Cheng et al. filed their patent application, this explanation had not yet been published. Should its publication affect the scope of the protection offered by their patent? I do not think it should, since subsequent explanations of what was surprising at the time an invention was made do not make it obvious either, but even so, it remains an intriguing question.

In another patent mentioning Cheng as inventor (1997), the quantity of inert gas used in deodorization is reduced even further by supplying this inert gas intermittently. This is most surprising indeed since according to the physical chemistry I was taught, the volume of stripping medium at stripping conditions determines how low you can get in volatiles. This is also reflected in the Bailey equation, which does not refer to the rate of supply or its interruption. So although the findings of this patent are in conflict with its theoretical basis, it was granted; a year later, the patent was allowed to lapse.

The third patent claiming the use of nitrogen as stripping medium (Krishnamurthy et al. 1992) specifies quite a number of process conditions. It must be of vegetable and/or animal origin, deaerated, heated to within a specified temperature range, and treated countercurrently at atmospheric pressure with nitrogen in a packed column with a specified surface-to-volume ratio for at least 5 min at a specified oil-to-gas weight ratio of 1.2 to 4.5, after which the oil must be cooled. Apart from the fact that operating at reduced pressure uses much less nitrogen,[4] the claim is easy to circumvent. Is there really so much prior art that had to be taken into account? In subsequent claims that depend on the main claim, hydrogenation prior to deodorization is included, whereby this hydrogenation should not lead to a relative decrease of the unsaturation of more than 0.3–1.3%; these are even easier to circumvent.

In 2004, Copeland et al. filed an application[5] that discloses the use of a non-condensable inert gas wherein this non-condensable gas is recovered and recycled in one or more deodorizing steps. The main claim specifies a temperature greater than about 375°C, but since claim 3 mentions 375°F twice, the degree centigrade should be regarded as a typing error by majority vote, especially since claim 7 mentions the most unlikely temperature of 470°C. The application was abandoned by failure to respond to an office action, but even so, the process sounds pretty hopeless to me. You may start with pure nitrogen, but since air leaking into the deodorizer is also recovered and recycled, the stripping medium will contain more and more oxygen, which will cause the oil to deteriorate.

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[4] The amounts given correspond to 180–660 Nm^3 per ton of oil. This sounds a lot and it certainly weighs and costs a lot, but using 1.0% of steam at 4 mbar and 240°C corresponds to some 7,000 m^3 per ton of oil.

[5] Earlier applications mentioning Copeland as inventor (vide infra) were filed by IP Holdings L.L.C., a company aiming to make money from patents. I just wonder why this company was no longer involved in Copeland et al. (2004b).

Neutralization by thin-film flash evaporation was disclosed by Chrbet and his wife[6] (1997). They operated at a temperature of 180–250°C and a pressure of 200–1,000 Pa (2–10 mbar). The European application was not pursued and the other East European applications were also allowed to lapse. The state of the art only quotes three Raffaetà patents, but it makes me wonder: Is there really no laboratory experiment where oil has been treated under those conditions? If so, its publication would have constituted prior art. Operating the flash evaporation at a lower temperature (160–200°C) and therefore at a lower pressure (0.003–0.08 mbar) has the advantage that carotene and vitamin E are retained in the oil being processed (Unnithan 1998). Patents have been granted in various countries (15 family members), and their ownership has been transferred to Global Palm Products Sdn Bhd, which has maintained them, at least in those European countries where they were in force.

Now we come to one of the major developments in vacuum stripping development: the SoftColumn® by Alfa Laval (Stenberg 1996; Stenberg and Sjöberg 1996; Hillström and Sjöberg 1998). It comprises a packed column through which the oil to be stripped flows downward by gravity while the stripping medium flows upward. Underneath that column, a number of trays with special valves (Hillström 1997) allow the apparatus to operate semicontinuously. These trays as well as the heat exchanger vessel (Sjöberg and Hillström 2000) are sparged with stripping medium, which is subsequently fed to the column. The vessel contains U-tubes to heat or cool the oil, and since similar tubes have been claimed in a subsequent Alfa Laval application (Gullov-Rasmussen 2008b), it was only to be expected that the former would be quoted as prior art for the latter in the equivalent PCT application.[7]

By operating countercurrently, the apparatus makes a very efficient use of the stripping medium. To allow the amount of this medium to be calculated, I worked out a formula (Dijkstra 1999)[8] that besides the usual variables, such as system pressure, vapor pressure of the pure volatiles, and initial and final concentration of the volatiles, also contains a parameter that is typical for the countercurrent process: the number of transfer units of the packed column. I defined this unit as the height of column required to ensure that the volatile content of the vapor leaving the unit at the top equals what it would be if it were in equilibrium with the volatile content of the liquid leaving the bottom of this unit. The paper shows that when the number of transfer units increases, the stripping medium requirement to achieve the same as a cross-flow system decreases to about a third of what the latter system needs. I would have loved to have used my formula to determine the number of transfer units of the SoftColumn® or any packed column experimentally, but no suitable opportunity arose.

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[6] They come from Slovakia and their English is charming. Cooling by heat exchange with incoming oil is described as follows: "Gained oil is cooled down to 60°C so that it hands over its heat to the entering oil."

[7] This is WO 2006/118517.

[8] I retrieved this article through http://scholar.google.com/advanced_scholar_search and saw that it has been quoted just twice. Big deal. On the other hand, the article I wrote with D. Meert (1982) on using inductively coupled plasma emission spectroscopy for the determination of trace elements in triglyceride oil and that forms the basis of current Official Methods Ca17 (01) and Ca20 (010) of the AOCS has been quoted only 16 times. So much for the citation index.

The SoftColumn® was introduced when people started to get worried about even negligible amounts of *trans* fatty acids. So the short residence time in the column was argued to be an advantage. On the other hand, a small air leak may cause air to pass through the column and rapidly cause double bonds to isomerize. In this context, the final Alfa Laval patent concerning the SoftColumn® (Hillström 2000) is quite relevant. It discloses a system to monitor how much air is leaving the vacuum system. With respect to the short residence time, I subsequently came to the conclusion (2007) that oil needs a certain heat treatment for the thermal breakdown of flavor precursors that are typical of its agricultural origin.

Such a heat treatment is given to oils before they are deodorized in a process disclosed by Van Dalen et al. (1994). They first treat the oil with a degumming acid; remove the gums, for instance, by first adding silica hydrogel, drying, and filtering; and then, preferably after having added a fruit acid, keep the oil at an elevated temperature (preferably 60–160°C), before deodorizing the oil at a low temperature, which, according to claim 7 in the application, "is 30–180°C, preferably 60–160°C." However, in the granted European patent (0 672 096 B1), this claim has disappeared and claim 7 has been replaced by claim 8 from the application. New claim 8 is former claim 9, but still reads, "Method according to claim 8 …." New claim 12 also refers to itself. Time to have a look at the German and French versions of the claims. In the German version, new claim 8 refers correctly to claim 7 and new claim 12 refers correctly to claim 11, but the French version has the same typing errors as the English version. These things happen[9] and I fear they will continue to happen.

The Alfa Laval application (Gullov-Rasmussen 2008a) is specifically concerned with this heat treatment and discloses a tray design that creates a plug flow to ensure uniform thermal exposure of the oil being deodorized. A later Alfa Laval patent application (Ng 2007) is concerned with heat recuperation. It discloses the incorporation of a heat exchanger in which the fatty acid distillate (FAD) that has been condensed in the scrubber section of a deodorizer is used to heat up refined oil to be fractionated or winterized.

Another inventor who is concerned about *trans* isomer formation is Copeland, who together with Belcher disclosed a dual-temperature deodorization process in 2001. In addition, they are concerned with tocopherol recovery expressed as wt% tocopherol in distillate. Table 9.1 is a copy of Table VI in Copeland and Belcher (2001) with three additional rows.

One of these additional rows calculates how much tocopherol the distillate contains, another how much tocopherol should therefore have been left in the deodorized oil, and the last one how much tocopherol is not accounted for. Accordingly, this table shows that the examples demonstrating the beneficial effect suffer from large tocopherol deficits and are therefore anything but convincing; this has not prevented the various Examiners from granting a patent.

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[9] Having been active as the editor of various books may have provided me with a keen eye for this kind of mistake.

Table 9.1 Tocopherol mass balance according to Copeland and Belcher (2001)

Temperature first tray (°C)	246	266	266
Temperature second tray	246	266	246
Tocopherol in feedstock (ppm)	1,263	1,263	1,201
Distillate as wt% of feedstock	0.15	0.15	0.18
Tocopherol as wt% of distillate	11.17	13.19	14.50
Tocopherol in distillate as ppm in feedstock	168	198	261
Tocopherol in feedstock minus tocopherol in distillate (ppm)	1,095	1,065	940
Tocopherol in deodorized oil (ppm)	1,080	721	804
Tocopherol unaccounted for (ppm)	15	344	136

This dual-temperature stripping certainly worried De Smet Engineering since they also wanted to claim this, albeit for different reasons. So the application (Kellens and Harper 2002)[10] filed on 14.05.2001 includes dependent claim 5 specifying that it "incorporates two or more deodorization sections operating at different temperatures." However, by tying this dependent claim to something novel (the location of the scrubber in the lowest part of the deodorizer, which has the mechanical advantage of reducing the thermal strain on the deodorizer vessel), the combination was novel as well and therefore permitted. In fact, the Search Report did not even list an earlier patent application (Copeland and Belcher 2000)[11] published on 02.06.2000, despite the fact that it mentions dual-temperature deodorization.

Another application by Copeland and Belcher (2003) introduced dual-temperature scrubbing. In the high-temperature scrubber (165–232°C, and preferably from 188 to 199°C), tocopherols and sterols will be preferentially condensed, whereas at the low temperature (38–77°C, or preferably 54–60°C), the fatty acids and all remaining volatiles will condense. The scrubber temperatures are maintained by controlling the temperatures of the circulating condensate. Not surprisingly, the application by Kellens and Harper (2002) was quoted as prior art. In Europe, the patent was granted but allowed to lapse soon afterward.

This application was not quoted in yet another application claiming dual condensation (Kruidenberg 2003) because the former was published on 20.11.02, which is after the priority date of 23.07.01 of the Kruidenberg application. However, this date is later than the publication date of an article by Petrauskaitè et al. (2000) that was quoted as serious prior art (with an "X") by the EPO. The Search Report in Kruidenberg (2003), which was compiled by the USPTO, did not mention this article. Instead, and after a divisional application, it eventually granted an apparatus patent (US Patent No. 7,597,783) on 06.10.09 and the accompanying process patent

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[10] By this time I was working for De Smet on a freelance basis, and this is one of the first applications I drafted for this company.

[11] Having already given some attention to "organic refining" in Chapter 5, I am not going to describe what subsequent applications and patents arose from this first effort. It would take several pages and waste even more money.

(US Patent No. 7,598,407) on the same day. In the US, a further continuation has been filed as (Kruidenberg 2010), but in Europe, the application is still pending.

The file wrapper of the US application includes a "List of references cited by examiner" and also a "List of references cited by applicant and considered by examiner." Both are dated 20.04.07, which is later than the EPO Search Report was published. Surprisingly, the list cited by applicant does not include Petrauskaitè et al. (2000). I say "surprisingly" here since US patent law lays down a Duty of Disclosure:

> "Each individual associated with filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section."[12]

So if a party who finds this patent a hindrance were to bring this omission to the attention of a court, that court would probably rule that "all claims are rendered unpatentable or invalid"; it would not limit itself to just those claims that are affected by the prior art that was not reported.

The dual condensation systems disclosed by Kellens and Harper (2002), Copeland and Belcher (2003), and Kruidenberg (2003) have the disadvantage that the vapors leaving the deodorizer have to pass through two vapor scrubbers before their incondensables reach the vacuum system. These scrubbers constitute a resistance, so there will be a pressure drop, causing the pressure in the deodorizer to be higher than nearer the vacuum pump. Packed columns as disclosed in Hillström and Sjöberg (1998) also cause such a pressure drop and thereby increase the stripping medium requirement. In an application disclosed by Kellens and de Suray (2005), a steam ejector is inserted in between the trays and the packed stripping column. The partially stripped oil flows by gravity from the column onto the trays that are sparged with steam. The vapors leaving the trays are collected by a small steam booster pump and are fed under the packed column together with the motive steam.

Having been personally involved in the drafting and prosecution of this patent, I had a look at how it had fared. In Espacenet I saw on the *Bibliographic data* tab that the patent "had also been published as": and then several patents were listed. The tab leaves limited space for this list, so when there are many equivalents, only a few (five?) are listed. To find more, you have to click *View INPADOC patent family* on that tab. I did and read that the family consisted of four applications/members. However, when I went back to the *INPADOC legal status* tab, I saw that there were more than four members still in force. I now understand why the following is true:

> "The EPO does not accept any responsibility for the accuracy of data and information originating from other authorities than the EPO; in particular the EPO does not guarantee that they are complete, up-to-date or fit for specific purposes."

So it is prudent to consult the patent registry from different directions and hopefully avoid its shortcomings that way.

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[12] This is a quotation from http://www.uspto.gov/web/offices/pac/mpep/mpep_e8r5_2000.pdf. It is very useful to be able to consult the rules of the game from my desk in France.

Another De Smet application I wrote (Kellens and De Greyt 2006) is concerned with the deodorization of cocoa butter. This fat releases theobromine and caffeine during vacuum stripping, and these compounds tend to solidify in the scrubber. By extracting the condensate with water, solid deposits are effectively prevented. Patents were granted in Europe and the US without much ado. The latest De Smet application concerning deodorization is (Kellens and Harper 2008). Like an earlier application by the same inventors (Kellens and Harper 2002), it offers mechanical advantages over the prior art. Fitting a structured packing inside a cylindrical vessel requires careful cutting of packing elements to avoid channeling. An example of such a structured packing has been disclosed in Bühlmann (2001). Fitting the same elements in a rectangular housing is far easier and cheaper. Moreover, evenly distributing a liquid over a rectangular surface is also easier than over a circular surface. The rectangular[13] housing is fitted inside the cylindrical deodorizer vessel, and this leaves four segments in between the housing and the vessel wall that can act as vapor ducts that then also act as thermal insulation and hopefully improve the performance of the packed column. Again, patents were granted in Europe and the US, but the latter needed quite some convincing before granting a patent. This again illustrates that patents are national affairs.

9.3 Miscellaneous Processes

Do you want a soybean oil with a peanut oil flavor? Then you should operate the process disclosed by Kuss (1991). You take peanut oil, heat it, and blow an inert gas through it that strips out some characteristic flavoring compounds. If you then conduct this gas stream through cold soybean oil, this will acquire a taste of peanut oil. Presumably, you can still sell the deodorized peanut oil as such and the flavored soybean oil at a premium.[14] The process takes at least two hours since Kuss operates at atmospheric pressure. If he had reduced his pressure, he would have saved on inert gas. The process can also be used to provide soybean oil with an olive oil flavor. However, not everybody likes that flavor, and so Van Buuren et al. (1999) disclosed a deodorization process for olive oil that gets rid of the odor but retains at least 1,500 ppm of squalene and most preferably at least 200 ppm of polyphenols; the resulting oil is used in a spread.

Color is more difficult to transfer than odor, but you can concentrate and retain it. Ibuki et al. (1995) disclosed a low-temperature steam stripping process of an oil with a high carotene concentration. Solvent fractionation is a means to arrive at such an oil so that the oil will not be cheap. Perhaps that is the reason why subsequent inventors Hashim et al. (2010) characterize their process as a *commercial process*

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[13] In practice, it will, of course, be square, but to avoid loopholes, it was described as tetragonal and specified as square in a subsequent claim.

[14] Not surprisingly, the patent originates from a consumer goods company.

for the production of refined palm oil rich in natural carotene. They also fractionate palm oil, take the olein, and then degum, neutralize, wash, and deodorize it in such a way that they retain at least 75% of the carotene. I can understand why they prefer chemical neutralization to physical refining, but by specifying a separate degumming step, they invite infringement. Omitting the degumming step will cause any gums present to be removed during the chemical neutralization step and should therefore work just as well.

Another patent that is easy to infringe is (Zwanenburg et al. 2000). It prescribes exposing the oil to an aqueous solution of ascorbic acid before the oil is deodorized. The ascorbic acid causes peroxides to be reduced so that the deodorized oil shows a low peroxide value. However, bleaching the oil and the heat treatment inherent in deodorization also decompose peroxides, so analyzing an oil and noting a low POV cannot reveal its cause and therefore does not prove infringement. Instead of exposing oil to an aqueous solution of ascorbic acid, Sampalis and Massrieh (2009) wash their fish oil with aqueous hydrochloric acid before treating the oil with activated carbon and stripping the oil under vacuum. Fish oil is also reported to benefit from the presence during deodorization of 0.1–0.4% deodorized rosemary or sage extract (Kendrick and MacFarlane 2000). If so desired, ascorbyl palmitate and mixed tocopherols can also be added.

One of the shortest patent applications I have come across (Zimmer 2006) covers just one and a half columns. It states that on heating, oils that contain water tend to get damaged by light and oxygen. Accordingly, it prescribes that oil is stored under nitrogen and shielded from light when it is heated to remove the water by evaporation. Another outstanding feature of this application is that it refers to the Ayurveda, where this heating process is referred to as ripening. I doubt if a patent will ever be granted since industrial dryers tend to be metal vessels that do not transmit any light.

Because diglycerides (diacylglycerol or DAG) are considered to be less fattening than triglycerides, a need to purify them has been perceived. They are produced by the glycerolysis of fats, which leads to an equilibrium mixture of triglycerides, diglycerides, monoglycerides, and glycerol, the position of which is determined by the temperature-dependent solubility of the glycerol. Removing the monoglycerides from this mixture can be by distillation, but care should be taken to prevent diglycerides from forming further monoglycerides (and triglycerides) during this distillation.

So Maruyama et al. (2006) prescribe that the diglyceride mixture to be purified should have a low transition metal content, which they achieve, for instance, by adding a chelating agent. Then the mixture is subjected to a countercurrent vacuum stripping process in a packed column at a temperature of 250–280°C to remove monoglycerides and leave the DAG and the triglycerides. In another application dealing with DAG (Choo et al. 2007), these compounds are obtained in a short- path distillation process operating at a vacuum below 0.01 mmHg.

Perilla oil is a seed oil with a high α-linolenic acid content. It can also contain perilla ketone, a lung toxin for livestock. According to Herrmann and Lang (2008), a ketone-free oil is obtained by vacuum steam stripping for 160 min at 180°C or for a shorter period when the temperature is a bit higher. The temperature should not be too high, to avoid *trans* isomer formation.

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Chapter 10
Hydrogenation

10.1 Introduction

The hydrogenation process of edible oils was invented by Wilhelm Normann in 1903, and he was also active in promoting its exploitation.[1] The process soon became very important since it converted liquid oils into the solid fats that were needed for margarine and shortenings, and it made perishable oils like fish oil or whale oil available for human consumption. The reason that I put the previous sentence in the past tense is not that whale oil is no longer available but that there has been a sudden drop in the amount of oil being hydrogenated because of the current *trans* scare.

Partial hydrogenation of unsaturated oils inevitably leads to the formation of *trans* fatty acids (Dijkstra 2006), and it does not matter whether this hydrogenation takes place in the rumen of a cow or in an edible oil refinery. However, in 1990, a paper was published (Mensink and Katan 1990) reporting on the effect on blood lipoprotein levels of feeding healthy people with a diet that contained a high percentage of *trans* fatty acids. It showed that such a diet would be rather unhealthy for rats. Given the cholesterol myth (Ravnskov 2000) and despite the lack of clinical evidence supporting the hypothesis that high-density lipoproteins protect the vascular system (Vergeer 2010), it is not surprising that *trans* fatty acids got such a bad name that they became virtually banned. After all, banning them also offered potentially rewarding marketing opportunities.

This is not the first time that fats that had been consumed for generations were all of a sudden banned. After World War II, it happened to oils containing erucic acid,[2] such as high erucic acid rapeseed oil (HEAR). It is one of the oilseed crops that can be grown in northern Europe, but all of a sudden, there were no more bright yellow fields in May. HEAR continued to be grown in China, though, and the oil that was

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[1] See "The battle over hydrogenation (1903–1920)" by G.R. List and M.A. Jackson at the *Lipid Library*: http://lipidlibrary.aocs.org/history/history.html.

[2] The website http://www.foodstandards.gov.au/_srcfiles/Erucic%20acid%20monograph.pdf gives a recent review.

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4_10,

Table 10.1 Life expectancies in the Netherlands and France (Taken from http://www.worldlifeexpectancy.com/history-of-life-expectancy)

	The Netherlands		France	
Year	Male	Female	Male	Female
1960	71.5	75.4	67.0	73.6
1970	70.8	76.5	68.4	75.8
1980	72.5	79.2	70.2	78.4
1990	73.8	80.1	72.8	80.9
2000	75.5	80.6	75.3	82.7
2010	76.9	82.3	77.9	84.4

banned in Europe continued to be part of the Chinese staple diet. So with more than 1.2 billion people left in China, this oil cannot have been that toxic.

Something similar holds for *trans* isomers resulting from partial hydrogenation. They have been part of our diet for generations, so if they were as toxic as we are led to believe, most of us would not be around since our parents or even grandparents would in all probability not have survived their regular intake of *trans* isomers. I know that this is a rather unusual way of looking at dietary fats and health. I have therefore tried to use the predictions made in articles about the number of lives that will be saved if people were to reduce their *trans* fat intake to calculate how many people should have died of cardiovascular diseases in the past because they consumed *trans* fats. If the number of people who actually died was less than should have died according to this calculation, it would refute these predictions.

I am most sorry indeed that it turned out to be impossible to make this kind of calculation because of what I could describe as a lack of a steady baseline. When you want to study an effect, you look for a change and make comparisons. If then the value used for the comparison tends to shift for no obvious reason, the comparison becomes meaningless. So we are left with the overall observation that eating *trans* fats did not cause mankind to die like rats. Rats may, but we don't. So instead I had a look at life expectancies in two countries that are rather similar except for the fat they eat. The Netherlands, home to Van den Bergh and Jurgens, is a typical margarine country, and its people have therefore been exposed to *trans* fats for generations. It also produces dairy products, but they are also exported to countries such as France, which has the highest per capita butter consumption in the EU (Dijkstra 2000). Table 10.1 shows that life expectancies are quite similar in both countries.

Given this *trans* scare, it is easy to predict that quite a few hydrogenation patents will disclose catalysts or processes that claim to produce partially hydrogenated fats with a reduced *trans* content.

10.2 Hydrogenation Processes Using a Nickel Catalyst

The priority date of Oudejans and Verzijl (1990) is 1986, which is before the *trans* scare alarm started sounding. Accordingly, the specification does not mention *trans* isomers at all. Instead, it discloses how to produce a catalyst that is so selective that soybean oil, when hydrogenated to an iodine value (IV) of 90, has a solid fat content at 30°C (N_{30})[3] of less than 2%. In Europe, the patent was opposed by Süd-Chemie and revoked in 1994.

However, *All documents* in Espacenet, reveals some oddities. There are three entries dated 25.03.1994 concerning the revocation of the patent. Then there is an entry dated 14.06.1999 summoning those concerned to an oral hearing, so I had a look at the original. That has a much earlier date of 14.06 1993 stamped on it. Similarly, the entry dated 16.01.2000 refers to a document dated 12.01.1990. Not surprisingly, there follows a final entry on 03.07.08 concerning a final clean-up of the Client Data Base. All this just goes to show that you should not believe everything you read.[4]

Another application that did not make it is Purves (1991). It was applied for in the US. Within a year, a PCT application was filed and subsequently, a European application was filed. The Search Report shows four Ys, “Documents of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.” I tend to agree and I am therefore not surprised that the application was withdrawn.

A somewhat later patent (Alouche et al. 1994) that is also concerned with the formulation of a hydrogenation catalyst starts by stating that it aims at maintaining the original *cis* bonds in vegetable oils. The catalyst comprises rare earth metal oxides in addition to nickel and optionally aluminum oxides. Two examples are given employing different catalysts according to the invention. One of them shows small decreases in all unsaturated fatty acids present in the rapeseed oil used as raw material and a substantial increase in the stearic acid formed. Elaidic acid is the only *trans* isomer formed. The other catalyst forms small amounts of polyunsaturated *trans* isomers, no stearic acid, and hardly any elaidic acid. Both products are claimed to be ideal lubricants, which is in line with the fact that the applicant is a petrol company. The patent has only been applied for in France. It was granted soon after application and allowed to lapse shortly after.

Another inventor who also aimed at a reduced *trans* formation (Higgins 2004) uses a commercial nickel catalyst and poisons it with phosphated mono- and diglycerides. According to the specification, the conditioning mechanism is not understood, but one possible mechanism could be that the conditioner “modifies the catalyst so that no or minimal active sites remain on the surface of the catalyst and it has a network of narrow pores which are the active catalyst sites. A catalyst having this structure means that the reaction is almost exclusively within the narrow pores.”

When the inventor compared the use of his conditioned catalyst with another method of reducing *trans* isomer formation, namely, lowering the catalyst concentration and thereby increasing the hydrogen concentration in the oil, he noted

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[3] This notation indicates that the patent has been applied for by Unilever. This company introduced this notation after having introduced the SFC measurement by pulse-NMR, but whereas the measurement was widely adopted, the notation was not.

[4] *Cf.* the Epilogue.

significant differences. Using less catalyst led to unacceptably long reaction times. Evaluating the invention is difficult because of the units used. They not only include lbs but also a hydrogen count of 235 scf; the statement that the refractive index measurement was 49.2 at 60.c on the butyro scale stopped my attempts to work out the extent of hydrogenation.

This brings me to a Cargill application (Van Toor et al. 2005) that I also find dismal to read. I know that patents never compete for literature prizes, but even so, specifications should be without typing errors, use the right words, and refrain from verbosity. Just look at this:

> [0013] . . . The unsaturated feedstock may then be contacted with the previously treated activated catalyst composition and hydrogenated by sustaining a hydrogenation reaction at a second temperature of no greater than about 700°C. In this embodiment the feedstock may comprise at least one polyunsaturated hydrocarbon.

The 700°C is a typing error. It should probably read 70°C since this is the value specified in the main claim. "Hydrocarbon" is the wrong word. It should probably read "fatty acid moiety." And the verbosity is atrocious. Why not just write, "The oil is hydrogenated at a temperature below 70°C while using a catalyst that has been liberated by melting its protective fat coating at a temperature above 100°C?" Because that is what the invention is about. Catalysts as supplied are embedded in a high-melting fat to protect them from oxidation. This fat must be melted away before the catalyst can act as such.

The patent of Van Toor et al. (2005) shows that the selectivity is very low so that the amount of stearic acid formed is high; moreover, the amount of catalyst used can be some 100 times higher than the amounts considered to be adequate at higher temperatures (Dijkstra 2006). Apart from being difficult to read, I find this patent rather useless.

A later application (Hassan et al. 2008), whose Search Report quotes Van Toor et al. (2005), also operates at low temperatures but avoids using large amounts of catalyst by first activating the catalyst at elevated temperatures. Example 1 employs an activation temperature of 150°C, which is apparently sufficient to cause the oxide film covering the nickel metal to react. Example 4 compares the activated catalyst with a non-activated catalyst, and the difference is quite large. Under the same experimental conditions, the non-activated catalyst caused an IV drop of 4.1, whereas the activated catalyst caused the IV to drop by 28.0.

In addition, the patent application (Hassan et al. 2008) discloses the use of high shear to increase the rate of hydrogen dissolution. In normal hydrogenation reactions, the concentration of the hydrogen in the oil is only a few percent of its solubility as long as the oil is still sufficiently reactive and has a linoleic acid content of, say, more than 20% (Dijkstra 1997). Since the rate of hydrogen dissolution is determined by the difference between the solubility and the concentration of the hydrogen in the oil and by the rate of agitation, it is clear that increasing the latter by introducing high shear will increase the hydrogen concentration in the oil. This will decrease the selectivity of the reaction, as is clearly shown by the examples in Hassan et al. (2008).

A method to control this selectivity and especially to control the extent of *cis-trans* isomerization has been disclosed by Colen et al. (1990) in an application that was only filed in the UK and withdrawn soon after it had been filed.[5] I think it is a very elegant method. The inventors realize that in the early stages of a normal, industrial hydrogenation run, the concentration of the hydrogen in the oil is so low that it is virtually impossible to change it. However, when the reaction mixture has become less reactive, this hydrogen concentration increases and starts to affect the various selectivities of the reaction. By measuring this concentration and controlling it within the limits displayed by previous batches, the reproducibility of the process is much increased.

According to the method (Colen et al. 1990), the extent of the reaction is monitored by measuring the total amount of hydrogen that has been consumed, and the concentration is determined by measuring the rate of hydrogen dissolution. So if the activity of the catalyst happens to be lower than usual, this causes the concentration to be higher than usual, which would lead to a hydrogenation product with different properties. Therefore, the method prevents this concentration from becoming higher by lowering the system pressure, and that is exactly the opposite of what an operator would have done. He would see that his reaction is slow and therefore needed speeding up. He would have tried to get it back to normal by increasing the hydrogen concentration by allowing the system pressure to increase. In doing so, he would have lowered the selectivity of the hydrogenation.

A method to control continuous hydrogenation reactions has been disclosed by Rivers Jr. (1990). The method involves measuring the viscosity of the oil to monitor the iodine index, and the opacity to monitor the Solid Fat Index of the hydrogenation product. The control system comprises a hydrogen nozzle sparger and a vibrator for said sparger causing the hydrogen bubbles to be reduced in size. A European patent was also applied for, but it was refused.

Lee et al. (2001a) stress that partially hydrogenated polyunsaturated oil contains conjugated linoleic acid (CLA), which they characterize as “an unsaturated fatty acid of 18 carbon atoms that is known as having an excellent efficacy, such as lowering of a blood cholesterol concentration in an adult, a reduction in body fat, an anticancer function and the like.” They do not mention that their CLA contains a *trans* double bond and should therefore be banned. Their application is not so much about how to generate the most CLA but about the avoidance of the typical hydrogenation odor. They do this by adding an antioxidant to the bleached oil before this is hydrogenated.

In another patent (Lee et al. 2001b), the inventors disclose another method to avoid these hydrogenation odors. They bleach with two adsorbents: a bleaching earth to get rid of pigments and a second adsorbent selected from the group of magnesium silicate, silica, and silicic acid to get rid of odor precursors. Two other Korean

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[5] I once asked one of the inventors if he knew why this most elegant of methods had not been pursued. He told me that this was because Unilever withdrew from edible oil processing. He also told me that the method had continued to be used at the Unilever plant in Purfleet, UK, and that it worked very well.

inventors (Jung and Choi 2009), who are also very much concerned with smell, disclose that deodorizing the oil before hydrogenating it under mild conditions results in a hydrogenated product with a low *trans* content and a buttery flavor that is 100-fold stronger than normal. Because the application claims a low *trans* content, it also lists how bad these isomers are. Surprise, surprise: "Heavy intake leads to obesity." When highlighting remarkable aspects in the conclusions, I noted that the hydrogenation catalyst was removed by using filter aids selected from the group consisting of . . . salicylic acid. It took me quite some time to guess that they meant silicic acid.

10.3 Processes Using Other Catalysts

I want to start this section by discussing a number of patents that can use both nickel and other catalysts. After having filed two priority documents in Sweden, Härröd and Møller[6] filed a single PCT application (Härröd and Møller 1996) that eventually led to a family of 24 applications, including two US patents (Härröd and Møller 1999, 2001). In Europe, a patent was granted but opposed by Thomas Swan & Co. Ltd., Consett, UK, a family-owned chemicals company and Evonik Degussa GmbH, Hanau, Germany, a custom design catalyst manufacturer. The patent was revoked in 2006, but this decision was appealed and there were further hearings in 2008 as a result of which it was decided that

> "The decision of appeal is set aside. The case is remitted to the Opposition Division for further prosecution on the basis of the claims according to the third auxiliary request submitted under cover letter dated 14 March 2008 (now main request)."

Nothing much happened, so the patent owner "requested acceleration of the opposition procedure." The opponents were then given 4 months to present their request, but they did not reply. So on 26.01.11 the Opposition Division concluded that the subject matter of the new main request was novel and based on an inventive step. The proprietors were requested to adapt the description to the new main request, whereupon opponents will be given the chance to comment on the amendments. Should there be no objections to the amended description,[7] the decision to maintain the patent in amended form will be issued.

So what is the patent about? In its original form, it covered the hydrogenation of triglycerides or fatty acid methyl esters to produce fatty alcohols, and oxygen to produce hydrogen peroxide. Unity of invention was presented by specifying that the substrate, the hydrogen, and a solvent were to be brought to a homogeneous supercritical (or near-supercritical) state and that this mixture was to be contacted with a catalyst.

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[6] Given their foreign names, it is not surprising that the USPTO came up with a number of variants: Møller was also mentioned as Moller and Möller and Århus as Aarhus (Sweden) and Arhus (Denmark).

[7] Presumably, opponents can still object to the amended description. I do not know what will happen then, but it will certainly take time. The earliest priority date is 01.07.94, and in early 2011, the matter had still not been fully resolved.

The main claim also specified that the reaction products form a constituent in the supercritical solution, but the reason for this additional limitation is not clear to me.

In standard industrial hydrogenation processes, the solubility and therefore the concentration of the hydrogen in the compound to be hydrogenated limit the rate of reaction. In the case of the hydrogenation of triglyceride oils, they are also responsible for the various selectivities (Dijkstra 2011). However, when the substrate is dissolved in a solvent that is completely miscible with hydrogen, the hydrogen concentration is very much higher, which drastically changes the rate and course of the reaction. An unselective hydrogenation results, and when selectivity is aimed for (Härröd et al. 2005), the rate advantage is no longer there (Sect. 4.2.6.4 in Dijkstra 2007). In fact, the high rate of reaction and the lack of selectivity made the super- or near-critical hydrogenation process suitable for full hydrogenation, but as far as I am aware, the process has not been applied industrially.

The fact that Evonik Degussa opposed the Härröd patents is not surprising since Degussa AG was working on continuous hydrogenation in supercritical media itself: (Tacke et al. 1995) granted in the US under number 5,734,070. This is also illustrated by this PCT Application being listed in the granted US patent (Härröd and Møller 2001). I will not go into detail about the subtle differences between the two patents since the processes have not been applied industrially anyway (R.F. Ariaansz, personal communication, 2010). The supercritical hydrogenation of a wide range of organic compounds was disclosed by Poliakoff et al. (2000), the prior purification of the substrate by extraction with a condensed fluid was disclosed by Tacke et al. (2001), and the use of noble metal colloids for the hydrogenation of fatty acids was disclosed in (Tacke et al. 2000). Not surprisingly, the Degussa patents concentrate on the use of platinum group metals.

At Vandemoortele, we were also concerned about *trans* formation, and when I came to the conclusion that this was inherent to the hydrogenation mechanism, Van Steenkiste in my department came up with the idea to use zeolites with micropores that would admit straight *trans* fatty acids but exclude the curved *cis* acids. If the location of catalytically active sites could be limited to inside those pores, it should theoretically be possible to selectively eliminate *trans* bonds from a partially hydrogenated fat. So we contacted a zeolite specialist at Leuven University, who agreed to undertake some experimental work with zeolites that were partially coated with platinum.

The idea was found to work and led to a patent application (Jacobs et al. 1998). A patent was granted in Europe (EP 0 917 561) to the university where the work had been done since by then Vandemoortele had sold its refineries. The patent was not opposed and was validated in several European countries until 2010, when no more fees were paid. Work in this field at the university has continued and led to a further patent application (Jacobs et al. 2004)[8] and two publications (Philippaerts et al. 2011a, 2011b).[9]

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[8] The applicant in this instance is UCB, a Belgian pharmaceutical company, and the subject matter of the application is far removed from edible oils and fats. The family list consists of 10 members, including European patent 1 587 620 that was granted on 09.09.09 and that has not been opposed.

[9] Ms. Philippaerts also presented a paper ("The shape selective hydrogenation of FAMEs and vegetable oil") at the AOCS Conference in Phoenix, 2010, where she won the Processing Student Excellence Award.

Precious metals were also used by Beers and Berben (2009), who disclose a process using nanoparticles of these metals or clusters of these particles. They obtain these particles by the reduction of precious metal ions in the presence of a bonding polymer that is selected from the group of aromatic polymeric materials containing at least one hetero-atom in the aromatic group such as polyvinyl pyrrolidone. In an example, soybean oil is hydrogenated to an IV of 70, which causes the C18:0 content to increase from 4.3% to 25.9%, with the *trans* content increasing from 2.2% to 4.5%. When the oil was brush-hydrogenated to an IV of 110, the stearic acid increased to only 9.9% and the *trans* content increased by only 0.7%. Given the high price of platinum and the cost of incomplete catalyst recovery, it is not likely that it is used industrially.

Copper catalysts are less expensive and are remarkable in that they hardly catalyze the hydrogenation of monoenes (Dijkstra 2002). In 1991, Henkel KGaA[10] applied for a patent (Gritz and Göbel 1992) disclosing the use of a copper/zinc catalyst. According to the examples, this catalyst is more selective (produces less stearic acid) than a commercial manganese-modified copper catalyst. Accordingly, a hydrogenation product with 86% monoenes and only 1% linoleic acid results. However, the application does not reveal the *trans* content of this product. The non-payment of the 1994 annuity caused the application not to be pursued.

Multiple consecutive uses of a copper-chromium catalyst were disclosed by Sleeter (2004). Table II in this patent gives the fatty acid composition of an olein and stearin obtained by fractionating a hydrogenation product. It allows the *trans* isomer content of this hydrogenation product to be calculated as 38.6% and the C18:1 content as 68.7%. This product also contains 14.3% residual C18:2 that will be partially responsible for the *trans* content. Accordingly, the *trans*/*cis* equilibrium has not been reached.

In a subsequent patent application (Sleeter 2008), the inventor treats a "first composition containing at least two sites of unsaturation" to arrive at a hydrogenated composition in which the ratio of the monounsaturated fatty acids to the saturated fatty acids is greater than 2 and the saturated fatty acid content is not substantially higher than in the starting material. This struck me as a complicated way to describe the prior art, so I checked its status via the *Public PAIR* system and was not surprised to read that the application had been abandoned for failure to respond to an Office Action.

Orange roughy oil is not a triacylglycerol but an ester between a fatty acid and a fatty alcohol. When this ester is hydrogenated using a copper-chromium oxide catalyst, the polyunsaturated fatty acids are hydrogenated to monounsaturated acyl moieties. According to the analytical results published in the application, all fatty alcohols in orange roughy oil are either saturated or monounsaturated, so that the alcohol moieties presumably do not participate in the hydrogenation reaction. Since the percentage of polyunsaturated fatty acid moieties is fairly small (4.3%), the *trans*

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[10] This company, dating from 1876, was split in 1999 into a consumer part and an oleochemical part called Cognis that was eventually taken over by BASF.

content of the hydrogenated oil is likely to be small. So its physical properties will have hardly changed, whereas its oxidative stability will have greatly improved.

Finally, I want to discuss two electrochemical hydrogenation processes. For background information on this kind of process, I refer to Pintauro (2011). Both the anodes and cathodes in the solid polymer electrolyte (SPE) reactor (Pintauro 2001) can use precious metal compounds such as Pd-black, Pt-black, or RuO_2 but can also use Raney nickel, Raney copper, or Raney nickel molybdenum alloy. The examples show that the hydrogenation hardly causes any *trans* isomer formation but that on the other hand, selectivities are very low. Some data in Table 6 of Pintauro (2001) indicate a linoleic acid selectivity < 1, meaning that oleic acid reacts faster than linoleic acid.

In another electrochemical hydrogenation process (Lalvani and Mondal 2004), a formate electrocatalyst is used as a mediator providing hydrogen atoms to the fatty acid being hydrogenated. The fatty acid profiles shown in the figures show a better selectivity than reported in the previous patent and low *trans* isomer contents.

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Chapter 11
Interesterification

11.1 Introduction

Although the ester interchange[1] or interesterification reaction had already been observed in the nineteenth century (Friedel and Crafts 1865) and was the subject of three patents in the 1920s (Grün 1922; Normann 1924, 1925), it took until after World War II before this reaction was first used for the modification of edible oils and fats. In the US, the plastic range of lard was extended by randomization (Vander Wal and Van Akkeren 1951) or by directed interesterification (Holman and Going 1959), and in Europe, this modification process was used to prepare special hardstocks for health margarines. Both processes used chemical catalysts such as sodium methanolate, sodium metal or its alloy with potassium metal, or the condensation product of sodium hydroxide and glycerol (Keulemans and Smits 1986).

Sodium methanolate is also the catalyst of choice to produce biodiesel (FAME) by the transesterification of triglyceride oil with methanol, but other catalysts such as potassium hydroxide are used in this process as well. The use of enzymes for biodiesel production has also been disclosed, but since non-food subjects are outside

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[1] The nomenclature of the various reactions is far from uniform. When I worked in a polyester polymer plant, we described the reaction between dimethylterephthalate and ethylene glycol as an "ester interchange"; in the edible oil sector this is called an "interesterification." When this reaction takes place within a triglyceride molecule, it can be referred to as "intraesterification," but when this happens in a partial glyceride, it is called "acyl migration." Enzymatic interesterification can also be referred to as "enzymatic rearrangement" (Ten Brink et al. 2006).

The process to produce FAME by reacting oil with methanol is commonly referred to as "transesterification" but can also be called "methanolysis." Producing partial glycerides by reacting triglyceride oil with glycerol is usually called "glycerolysis." When the hydrolysis reaction to produce free fatty acids and glycerol is carried out industrially, it is called "fat splitting." "Acidolysis" refers to the replacement of a fatty acid moiety in a triglyceride molecule by another carboxylic acid, and esterifying a free hydroxyl group with a fatty acid is called "esterification," but "reverse hydrolysis" has also been used (Schneider et al. 1996). However, the process in which free fatty acids and partial glycerides present in a crude or degummed oil are esterified has also been referred to as "remediation" (Cowan 2011) or "reforming" (Matsuzaki et al. 1991).

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the scope of the present monograph, it will not be further discussed. It is interesting to note, though, that the sudden interest in biodiesel has led to a surge in interesterification R&D, resulting in a flurry of patents.

Enzyme interesterification catalysts were introduced (Coleman and Macrae 1980) for their specificity to produce 1,3-disaturated, 2-monounsturated triglycerides to be used as cocoa butter equivalents by interesterifying a high-oleic-acid vegetable oil with stearic acid or methyl stearate. Later, in response to the current *trans* scare, the enzymes started also to be used in less critical applications to produce *trans* isomer-free hardstocks for margarine and shortenings.

11.2 Fat Substitutes

Olestra (also known by its current brand name Olean®) was developed in the US by Procter & Gamble as a means to increase fat uptake in premature babies. Then it was promoted as a means to lower cholesterol uptake and finally as an indigestible fat substitute; because of this indigestibility, its consumption could lead to “loose stools” or “anal leakage.”[2] Chemically, Olestra consists of sucrose that has been esterified with six to eight fatty acids; as in triglycerides, the chain length and degree of unsaturation of these fatty acids determine the physical properties of the product. Olestra is made by the transesterification of FAME with sucrose (Rizzi and Taylor 1976, 1978).

Another fat substitute developed by P&G is caprenin. It is a normal triglyceride containing caprylic (C8:0), capric (C10:0), and behenic (C22:0) acids. Its calorific value is about half that of normal fats because the behenic acid is poorly absorbed in the body and because of the way that medium-chain fatty acids are metabolized. Caprenin was developed as a low-calorie confectionery fat. It was not produced by interesterification since this would have led to the high-melting tribehenin being formed as well. So the esterification of long-chain fatty acid monoglycerides with medium-chain free fatty acids was used instead (Kluesener et al. 1992). This esterification was carried out in the absence of a catalyst by heating the reagents to 140–250°C while removing the water formed by the esterification. Another way to introduce the medium-chain fatty acids in the monoglycerides was by reacting with an acid anhydride (Stipp and Kluesener 1992). Yet another way is to use randomization followed by a fractionation by molecular distillation (Seiden 1994) to increase the concentration of triglycerides with a single long-chain fatty acid.

A process to produce fatty acid anhydrides has been disclosed in Stipp and Kluesener (1995). It involves heating fatty acids with acetic acid anhydride and removing the acetic acid formed by distillation. This leads to mixed anhydrides, but by further heating and the distillative removal of acetic acid, these mixed anhydrides can be converted into fatty acid anhydrides. The patent also claims that the resulting

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[2] When my boss asked me if my department had an answer to Olestra, I answered, “Mr. Raymond, this is a typical P&G product since this company is big in detergents and Pampers.”

anhydrides contain less than 300 ppm of difatty ketones.[3] These compounds are apparently formed at high temperature, and their formation can be suppressed by purifying under mild conditions. Their formation can also be suppressed by adding glycerin to the esterification mixture (Guskey 1996). Later Yan et al. (2005) disclosed that adding water to a reaction mixture that is heated to produce conjugated di- or polyunsaturated fatty acids also suppressed the formation of difatty ketones.

Salatrim is the acronym for "*Short- And Long-chain Acyl TRIglyceride Molecules*." The product was developed by Nabisco as a confectionery fat. This company filed an application on 20 September 1989, but it took a large number of continuations and abandonments before a patent (Wheeler and Otterburn 1995) was granted. The patent discloses a fatty coating composition that comprises 70–90% of a diacetin fat, meaning a fat that comprises triglycerides with two acetyl moieties and a long-chain fatty acid, and 5–30% of what they call a "crystal modifying fat" that consists of triglycerides with only a single C_2 to C_4 acid moiety. It describes the way to prepare these triglycerides, which is by reacting partial glycerides with acid anhydrides. This way was known at the time, so the patent (Wheeler and Otterburn 1995) does not claim this method but limits its claims to the composition.

To me, the most interesting one of these Nabisco patents is Pelloso et al. (1995). Example 1 of this patent describes an attempt to interesterify a mixture of hydrogenated rapeseed oil and triacetin. It describes the failure of this attempt by reporting that only the hydrogenated rapeseed oil took part in the randomization reaction, whereas the triacetin did not react at all, so that no acetyl groups were introduced into the rapeseed oil triglycerides. The reason I find this most interesting is that it supports the so-called enolate mechanism of the interesterification reaction (Dijkstra et al. 2005).

This mechanism assumes that the catalytically active intermediate of the interesterification reaction is an enolate anion that results from the abstraction of an α-hydrogen atom from a fatty acid. In the case of the acetyl radical, this α-hydrogen is a primary hydrogen atom, which is less labile than the secondary α-hydrogen atoms on fatty acids with more than two carbon atoms. Accordingly, the acetyl moieties do not react, and the way to overcome the problem disclosed in Pelloso et al. (1995) is to add some tripropionin and/or tributyrin. These short-chain triglycerides have secondary α-hydrogen atoms and take part in the enolate mechanism. They also cause the triacetin to dissolve in the rapeseed/tripropionin mixture, which facilitates the participation of the triacetin in the reaction so that the final product also contains some acetyl moieties. The reaction product is not what would be expected statistically since the propionyl/acetyl ratio in the deodorization residue does not correspond to the mole ratio in the feed.

Eastman Chemical Company disclosed a process (Cherwin and Johnson Jr. 2000) in which low-calorie fats like the one described above can be made continuously by high-temperature interesterification using soap. The fraction containing triglycerides

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[3] In the literature, these compounds are also referred to as dialkylketones. They can be formed as byproducts of the interesterification reaction. They were apparently a hot topic since searching for "difatty ketones" at www.google.com/patents results in nine P&G patents being listed.

with one or two long-chain fatty acids is isolated from the reaction mixture by first removing the most volatile triglycerides with three short-chain fatty acids by distillation at a pressure of 0.1–10^{-3} mmHg. Subsequently, the low-calorie fat is obtained by distillation at a pressure of 5–200 μm. The condensate from the first distillation and the residue of the second are recycled. Another distillative separation process (Sparsø and Engelrud 2004) starts with a triglyceride mixture that hardly contains any triglycerides with three short-chain fatty acids. In a first step, triglycerides with one or two long chains are separated from those with three long chains, and in a subsequent step, triglycerides with one long chain are separated from those with two long chains. The temperatures are high and the pressures very low.[4] The patent was applied for in almost ten countries. It was granted in the US (Patent 7,1156,760) but withdrawn in Europe. In another patent application (Sparsø 2006), the production of diglycerides via a similar two-step distillation process is disclosed. This application did not even make it to the national offices and was withdrawn before entering the European phase.

Another type of fat substitutes was invented and developed by Arco Chemical, which at the time was a major producer of propylene oxide. The substitute consists of a propoxylated polyol backbone that has been esterified with fatty acids. Saturated long-chain fatty acids provide the fat substitute with the desired properties, but introducing them by esterification causes difficulties. To arrive at a low-hydroxyl value, an excess of these acids is needed during the esterification, and removing the excess after esterification by distillation causes blockages because of the high melting points of these acids. The process invented by Cooper (1994) solves these difficulties by esterifying the propoxylated polyol with C_6–C_{18} fatty acids and interesterifying the esterification product with triglycerides containing C_{20}–C_{24} fatty acids. In doing so, he introduced the long-chain fatty acids in the fat substitute. I don't think any product was ever sold. In Europe, the equivalent application (EP 0 594 428) led to a Search Report that did not reveal any damaging literature. A Communication with intention to grant (Approval) was sent to the applicant on 17.02.97, but then on 17.07.97, a communication was dispatched that the application had been refused; reason: substantive examination. Sadly, the files are not available in electronic form.

11.3 Chemical Catalysis

A paper (Liu and Lampert 1999) that describes how the color of the interesterifying reaction mixture can be used to control partial interesterification caused me to send a Letter to the Editor in 2000, demonstrating that mixing a non-randomized reaction mixture with a fully randomized reaction mixture leads to triglyceride compositions

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[4] The patent (Sparsø and Engelrud 2004) has been assigned to Danisco A/S, a company that has experience with molecular distillation to isolate monoglycerides. Danisco is now part of E.I. du Pont de Nemours and Company.

that are identical to partially randomized reaction mixtures. The control method was also published as a patent (Liu and Lampert 2001). An intention to grant a European patent was sent on 24.09.02 in which the applicant was invited to pay the fees for grant and printing, fees for printing additional pages, and fees for the translation of the claims. The applicant declined the invitation[5] by not replying and thereby lost his rights on 11.03.03.

A heterogeneous interesterification catalyst was developed by Engelhard Corporation[6] (Bayense et al. 2000). This company supplies the edible oil industry with hydrogenation catalysts and foresaw a decline in demand but an increased opportunity in interesterification catalysts. Such catalysts may have the advantage that no oil is lost by the formation of FAME; they do not require inactivation and can hopefully be re-used. According to the patent, the catalyst should comprise one or more oxides and/or oxy-salts of certain elements, whereby at least one of these oxides should have an optical basicity Λ of at least 0.5, and preferably between 0.5 and 0.9.

In Europe, the priority document had been filed in 1994 in the Netherlands, which led to a PCT Application (WO 95/16014) and a granted European patent (EP 0 733 093 B1) that was not opposed and was maintained for 7 years; it was allowed to lapse in 2001. Because my former department had good contacts with Engelhard De Meern, we were asked to evaluate their interesterification catalysts.[7] We were not very enthusiastic. The interesterification required high temperatures (200–250°C) and a long reaction time, and we noted the formation of appreciable amounts of partial glycerides (D. Meert, personal communication, 1995).

Another heterogeneous catalyst was disclosed by the Kao Corporation (Kaita et al. 2002). The title of the patent and the examples all refer to transesterification, but interesterification is also claimed in claim 7: "A method for producing an ester compound, which comprises transesterifying an alcohol, a carboxylic acid or an ester compound with a starting ester in the presence of the catalyst as defined in claim 1." Like the Engelhard catalyst, the Kao catalyst also requires temperatures >200°C.

Metal salts of basic amino acids have also been claimed as heterogeneous interesterification catalysts (Peter et al. 2005). The example mention zinc arginate as catalyst in amounts of 5% (Example 1) and 0.5% (Example 2). Both examples use a temperature of 125°C and take 8 and 3 h, respectively. The literature Search Report was favorable, but the applications in the US and Europe were not pursued.[8] It is not clear if this type of catalyst has been used industrially, but it seems to be unlikely.

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[5] Would that be because of my Letter to the Editor, which convinced him that blending is cheaper?

[6] This company is now part of BASF.

[7] I had a look at the BASF websites and did not find any reference to this catalyst.

[8] This may be because Prof, Peter, who assigned his many patents to himself, passed away.

11.4 Enzymatic Catalysis

I keep the reprints and photocopies that constitute my collected literature in folders that I store in a number of filing cabinets. I keep track of them via a software program[9] that also permits me to generate bibliographies. Thus, I have several folders for chemical interesterification and others for enzymatic interesterification. When preparing this section, I noticed that the enzymatic folder contained mostly journal articles and relatively few patents. So the references cited in these enzyme patents may contain a full page of "Other publications," meaning non-US patents and especially non-patent literature such as journals and textbooks (Lee 2008). Similarly, a journal article about the industrial uses of lipases (Hills 2003) that was written by somebody working in industry did not refer to any patents. Could it be that what was published by academia prevented processes from being patented? Let's therefore see what could be patented.

In a patent granted in 1991, Matsuzaki et al. disclosed a process to "reform" fats, meaning that they convert the partial glycerides present in an oil or fat into triglycerides by esterifying them with fatty acids. In diglycerides, the 1,3-isomer is favored over the 1,2-(or 2,3-)isomer, as a result of which the free hydroxyl group tends to be on the middle carbon atom of the glycerol backbone. So a strictly 1,3-specific lipase would not cause this free hydroxyl group to be esterified. Therefore, the inventors specify a combination of enzymes having different specificities. This difference applies not only to positional specificity but also to fatty acid specificity.

In a patent that was filed a year earlier but granted a year later, inventors with the same affiliation (Matsumoto et al. 1992) disclosed an interesterification[10] process. The specification starts by describing the fundamental problem of enzymatic interesterification: Too little water decreases the enzymatic activity and too much water causes hydrolysis. This problem is alleviated by the addition of 0.1–2% by weight of ethanol. The process can be used to incorporate fatty acids added as such or as an ester into triglycerides or to interesterify triglycerides. In Europe, the original applicant of Matsumoto et al. (1992) sold its right to Asahi Denka, but this company allowed the granted patent (EP 0 321 777) to lapse soon after it had been granted.

A lipase that has strong specificity for partial glycerides can be isolated from *Penicillium cyclopium* (Yamaguchi et al. 1993). It can therefore be used to remove these partial glycerides from triglycerides by hydrolyzing them (*cf*. Dijkstra 2007) but also to produce partial glycerides that are essentially free of triglycerides by esterifying glycerol with fatty acids. In Europe, Henkel and Unilever opposed, but the patent was maintained in amended form and then allowed to lapse by non-payment of annuities, first in Germany and then in the UK.

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[9] I use the program ReferenceManager, which is now run by Thomson Reuters; I am quite pleased with it.

[10] The title mentions "transesterification," but as explained before, this term is used today only to describe a process in which triglycerides are allowed to react with lower alcohols.

It was quoted as a reference in a US patent (Davies and Macrae 2001) that also illustrates an enzyme specificity that causes only a single hydroxyl group in a polyol to be esterified by a fatty acid. The enzyme exhibiting this specificity is a potato lipid acyl transferase also known as patatin. The esterification causes water to be formed, which is preferably removed by vacuum or pervaporation. In the US, the patent (Davies and Macrae 2001) has a single claim:

1. A process for deacidification of a monoglyceride containing free C2-C24 monocarboxylic acid as impurity which comprises contacting said monoglyceride with glycerol and a catalytic amount of patatin at a temperature of from 25°C to 50°C whereby said free acid is removed by esterification of the acid with glycerol.

This claim is similar to the last claim (claim 11) in the European equivalent (EP 0 906 445). The preceding 10 claims are concerned with the type of acid that can be used (straight chain, branched chain, saturated, unsaturated), the polyols, the enzyme, which can originate from a genetically modified yeast or mold, and the reaction temperature range of 10–90°C. To study this discrepancy between the US and Europe, I visited the USPTO website and saw that the US application had a “child” that led to an Application Publication (US 2001/0044140), which led to a patent (US Patent 6,613,551). Both the application and the patent list the same 11 claims as the European equivalent.

As has been explained elsewhere (Dijkstra 2007), enzymatic interesterification started with the preparation of symmetrical, monounsaturated triglycerides used as cocoa butter equivalent; *cf*. Coleman and Macrae (1980), Matsuo et al. (1981), and subsequent patents. Use was made of the 1,3-specificity of the lipase enzyme to replace unsaturated fatty acids by saturated fatty acids on the α-positions of the glycerol moiety in triglycerides that had a high monounsaturated fatty acid content on the β-position, such as, for instance, high oleic sunflower seed oil. Using a lipase from *Rhizomucor miehei* and a carefully controlled water content can even lead to a ratio of asymmetric enantiomeric triglycerides (POSt and StOP) that differs from unity (Chandler and Quinlan 1994). However, in enzymatic interesterification, partial glycerides are an inevitable intermediate product and since these partial glycerides are prone to acyl migration, the specificity of the reaction is far from perfect. Moreover, the EU Chocolate Directive prevented the use of interesterified fats in chocolate, so this early initiative came to nothing.

Instead, the process started to be used for the manufacture of fats for infant formulas. These fats have a high palmitic acid content at the β-position and can be produced (Quinlan 1997) by selectively replacing saturated fatty acids on the α-positions of a fat with a high trisaturate content such as palm stearin by unsaturated fatty acids. In another process (Wang et al. 2000), palm oil enriched in palmitic acid and oils containing linoleic acid, α-linolenic acid, arachidonic acid (C20:4), and docosahexaenoic acid (C22:6) are first randomized using a chemical catalyst. In a second step, the randomized product is interesterified with medium-chain fatty acids while using a 1,3-specific lipase. The use of an enzyme that can distinguish between conjugated long-chain polyunsaturated isomers has also been disclosed (Cain et al. 2003).

The earliest patent disclosing a continuous process for the interesterification of oils and fats employing immobilized lipase in packed columns is probably (Eigtved 1989).[11] After describing the immobilization method and the resulting product, the patent claims an interesterification method in which solvent-free melted fats are passed through a column of immobilized *Mucor miehei* enzyme. A later patent (Kokusho et al. 1993) claims a different enzyme that is isolated from a species of microorganisms selected from the group consisting of *Alcaligenes* and *Achromobacter*. This difference or the fact that the substrate is in solution is probably the reason why Eigtved (1989) is not cited as reference in (Kokusho et al. 1993). In addition to the enzyme source, the patent also specifies that the fat must contain 100–1,800 ppm of moisture before being fed to the enzyme column. In 2011, Cowan[12] introduced a novel enzyme (Callera™ Ultra, a *Callera antartica* Lipase B), to be used as esterification catalyst. He stressed the importance of water elimination to drive the reaction to low residual FFA content.

Subsequent patents dealing with continuous enzymatic interesterification are mainly concerned with avoiding enzyme inactivation. Packed silica gel has been disclosed for this purpose by Lee and Sleeter (2003), whose application is deemed to be withdrawn in Europe and was abandoned in the US in 2006. However, in the US, a further application was filed that claimed the benefit of the abandoned application; this led to (Lee 2005) and finally to US Patent 7,452,702. When discussing this patent in the background to their own invention, Ten Brink et al. (2006) argued that the exposure of the oil to the silica may have been all right on a small scale but turned out to be ineffective on an industrial scale. Their process therefore discloses a process in which the oil is exposed to an adsorbent and the oil/adsorbent dispersion is exposed to shear energy. The European patent (Ten Brink et al. 2006) was granted but opposed by Fuji Oil Co., as a result of which it was revoked. In the US, Application 2005/0019316 was abandoned for failure to respond to an Office Action. The use of moisture-free silica as a processing aid to prolong enzyme activity was disclosed by Dayton and dos Santos (2009); this application also describes and claims the use and mode of operation of multiple packed-bed reactors.

Treating the fat to be interesterified with one or more types of vegetable protein was disclosed by Binder et al. (2006) and with granular clay or granular carbon before treating the fat with the lipase by Lee and Wicklund (2008). Treating the oil with a chelating agent like citric acid or phosphoric acid and then treating the oil with a base before exposing a lipase to the oil has also been claimed (Pearce et al. 2007) as an effective way to prolong enzyme life.

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[11] Although this patent has a full page with corrections of typing errors, the title reading *miehe* instead of *miehei* has not been corrected.

[12] His presentation and others are available at http://www.soci.org/News/lipids-enzymatic-2011

Since none of the above methods will be perfect, enzyme life will be limited. The industrial enzymatic interesterification plant offered by De Smet-Ballestra copes with this limited enzyme life by using four reactors that are filled with immobilized enzyme in series. When enzyme activity drops below a set level, the reactor with the oldest enzyme charge is shut down, emptied and charged with fresh enzyme, and used as final reactor. Peters et al. (2007) use a single reactor and cause enzyme and substrate to flow countercurrently.

Enzymatic interesterification can also be combined with fractionation to reduce the saturated fatty acid content of milk fat (Dalemans 2009). In fact, the process comprises a first fractionation to provide a milk fat olein that is then interesterified using enzymes, whereupon the interesterified olein is again fractionated to yield an olein with less than 50% saturated fatty acids. The application was first filed with the European Patent Office on 29.10.07. On 24.10.08, thus within the priority year, applications were filed in AR, AU, CA, CN, JP, KR, MX, US, UY, and the WIPO. This application also designated the EPO.

On the basis of the European priority application, the EPO published this application on 06.05.09 (EP 2 055 195 A1), and it was withdrawn on 31.02.10. Since the EPO was also designated in the PCT application, this led to another application number (EP 2 157 867 A1) and publication date (03.03.10) for the same application.[13] Because this application also comprises fractionation, it is a good moment to move on to the next chapter.

However, there are also two Unilever applications (Zoet and Keulemans 1991; Davies et al. 1992) combining fractionation and interesterification that can be discussed at this stage. The first application (Zoet and Keulemans 1991) discloses a two-step fractionation process leading to a stearin, a mid-fraction, and an olein, followed by the interesterification of the stearin and the olein and the recycling of the interesterified product to the first fractionation step. Its literature Search Report shows two Xs, and the application was withdrawn early in 1993. The second application[14] (Davies et al. 1992) discloses a process in which the diglycerides present in the olein fraction resulting from a shea butter fractionation are enzymatically hydrolyzed and the resulting FFA are allowed to interchange with the monounsaturated (SOO) triglycerides present in the olein. The main claim lists 11 steps, of which the fractionation to obtain said olein is mandatory. It prescribes a temperature of preferably –10 to –15°C,[15] which implies a solvent fractionation process. The INPADOC family only lists the European application (Davies et al. 1992), which was withdrawn in 1995.

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[13] Presumably, Corman had to pay the European fees twice, which explains why it is uncommon for the EPO to publish the same invention twice.

[14] The specification is not well written. When discussing the dry degumming of shea butter in the example, it mentions an "acetic bleaching earth" instead of an "acid-activated bleaching earth." This is not a typing error, but a lack of comprehension.

[15] When describing a range, I always put the lowest values first. So I would have written –15 to –10°C rather than "preferably –10 to –15°C."

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Chapter 12
Fractionation

12.1 Solvent Fractionation

Whereas a review of the fractionation of edible oils and fats in the 1980s (Hamm 1986) questioned to what extent solvents were necessary, a later review by the same author (Hamm 1995) concludes that the dry fractionation process has been so greatly improved that it has superseded the detergent and solvent fractionation processes. It is therefore not surprising that only a very few patents involving the latter processes have been applied for during the last 20 years.

In the field of triglyceride fractionation employing solvents, UOP obtained several patents (Zinnen 1988; Ou 1990) for a process for isolating monounsaturated triglycerides from their mixtures by using its Sorbex® process. I had come across this process when attending an AOCS World Conference on Emerging Technologies (Gembicki et al. 1986) and subsequently contacted UOP. This resulted in a cooperation[1] in which we taught UOP the basics of edible oils and fats and how to analyze their composition, and UOP applied for these patents. I liked their process and their unbiased approach. Given the high investment required for the Sorbex® process installation and the concomitant financial risk of low plant occupation, Vandemoortele decided not to proceed with industrial application.

A patent[2] granted to Loders Croklaan (Harris et al. 1998)[3] was also applied for in Europe. It was granted, but my former employer opposed it after I left; I guess that

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[1] The fact that I worked in the chemical industry before getting involved with edible oils and fats greatly facilitated this cooperation.

[2] The last claim of this granted US patent reads: "Process according to claims 6 or 8, wherein . . . ." This is multiple dependence, and I thought this should not have been allowed. So I went to counsel and learned that the US Patent Office will allow multiple-dependent claims but will not allow a multiple-dependent claim to depend on another multiple-dependent. So a "9. Process according to claims 6 or 8 . . ." is perfectly acceptable in the US as long as neither claim 6 nor claim 8 depends on more than a single claim. Similarly, claim 10 is not allowed to read "10. The process according to any of claims 6 to 9 . . . ."

[3] The inventor is also the author of http://lipidlibrary.aocs.org/processing/solventfract/index.htm.

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
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this opposition was at the request of Fuji Oil to protect the interests of the joint venture Vamo-Fuji.[4] The opposition led to an amendment in which the last two claims, the product claims, were deleted. Shortly afterward, the patent was allowed to lapse. The patent itself is concerned with the asymmetric monounsaturated triglyceride content of confectionery fats. It discloses an enrichment method by solvent fractionation.

Another company operating a solvent fractionation plant was Karlshamns[5]. Thus, it is not surprising that this company also filed an application (Alander et al. 1999) for a process that it could carry out internally. The process aims at concentrating biologically active unsaponifiables by the removal of triglycerides via solvent fractionation. Accordingly, high-melting triglycerides are removed first, and then the remaining triglycerides as present in the olein may be hydrogenated to facilitate their removal by solvent fractionation. The Search Report of the application shows a fair number of Xs, but the claims as granted are the same as those applied for with the exception that the rather general claims specifying a use have been split into several, more specific claims.

Yet another company operating a solvent fractionation plant is Fuji Oil Co. In its application (Taniguchi et al. 2000), it discloses a way to accelerate the solvent fractionation process. The solution of the fat to be crystallized is cooled rapidly in a heat exchanger to a temperature that is just above the crystallization temperature before it is allowed to crystallize in the normal crystallizer vessels. The flow through the heat exchanger can be continuous and can be used to fill one crystallizer vessel after another. The patent was granted in the US (6,265,595), but in Europe, the application was withdrawn.

Loders Croklaan[6] also operates a solvent fractionation plant; in a recent patent application (Wijngaarden and Hiemstra 2009), this company disclosed[7] a fractionation process that starts as a dry fractionation process in which a melt is partially crystallized. It continues as a solvent fractionation process in that the crystal slurry resulting from the first stage is mixed with a solvent such as acetone, cooled, and separated. The process is claimed to be less sensitive to any water present in the acetone, and it also uses less acetone than current solvent fractionation processes. J-Oil Mills Inc. applied for a patent (Sadakane and Hara 2009) entitled, “Dry fractionation method…” However, the abstract reads, “… dissolving the oil-and-fat composition; and subsequently crystallizing the dissolved oil-and fat composition…” Is this a dry fractionation process?[8]

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[4] With Vandemoortele having shed its refining operations, this former joint venture is now Fuji Oil Europe.

[5] In 2005, this company merged with Aarhus United to form AAK.

[6] Formerly independent, then taken over by of Unilever, now belonging to IOI Corporation Bdh.

[7] I dislike it when a text makes statements like, “The palm oil olein has an iodine value (IV) of between 35 and 65, more preferably from 50 to 60.” By definition, palm olein has a higher IV than palm oil, thus >52.

[8] The PCT application has not led to a European application, so the only claims that have been published are in Japanese.

12.2 Dry Fractionation with Stationary Crystallization

During fractional crystallization, the latent heat of crystallization (about 200 kJ per kg of crystallized fat) is liberated and must be removed from the crystal slurry being formed. However, not all fats crystallize in such a way that they form a slurry that can be agitated and made to flow along a heat-exchange surface. Palm kernel oil is one such fat. Accordingly, it was customary to solidify palm kernel oil in trays passing through a cooling tunnel, take the solid blocks out of the trays and wrap them in filter cloths, place the wrapped blocks in the cage of a hydraulic press, and squeeze. This caused palm kernel olein to be exuded, so that unwrapping the squeezed blocks yielded a palm kernel stearin (Rossell 1985). This stearin has a lower oleic acid content than the palm kernel oil itself, so that on hydrogenation, less stearic acid is formed and the melting point does not rise above body temperature, as illustrated by Table 12.1. Consequently, this hydrogenated palm kernel oil can be used as a cocoa butter substitute.[9]

This process is extremely labor-intensive, and so it is not surprising that several automation attempts have been made. In 1989, Higuchi et al. disclosed a dry fractionation process in which the molten material to be fractionated was introduced into a filter press and cooled in situ. The patent does not specify the oil, and the examples use palm kernel oil and palm olein (“soft palm oil”). It was a cumbersome process because it required the filter cloth to be sealed before the molten material was pumped into the press. Because of its low throughput, the process was also quite expensive. To make more intensive use of the expensive filter press, Kuwabara et al. (1991) separated the cooling/crystallization stage from the filtration stage by

Table 12.1 Melting points of lauric oils and derivatives (Adapted from Dijkstra 2007; sources Rossell 1985 and Jayaraman and Thiagarajan 2001)

	Palm kernel oil (PK)		Coconut oil (CN)	
	Iodine value	Melting point [°C]	Iodine value	Melting point [°C]
Non-fractionated	17.5	28	8.5	24
Stearin S	7	32	4	30
Hydrogenated S	4	31	1.5	32
Hydrogenated S	0.4	35		
Olein O	24.5	23.5	10	
Hydrogenated O	1.0	41		

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[9] In confectionery fats, there are several grades:

- Cocoa butter equivalents (CBEs) are chemically very similar to cocoa butter by having a high (>80%) content of symmetrical monounsaturated triglycerides. They can be mixed with cocoa butter in almost all proportions without affecting the physical properties of the butter.
- Cocoa butter replacers (CBRs) can replace only a limited amount of cocoa butter in chocolate. CBRs commonly consist of a mid-fraction of a partially hydrogenated mixture of an oil like rapeseed oil and some palm olein that is at *cis-trans* equilibrium.
- Cocoa butter substitutes (CBSs) are fats like hydrogenated palm kernel stearin and do not tolerate any cocoa butter.

first making blocks and then crushing these to form a pumpable paste that was then fed into a filter press. They limited their process to non-lauric fats because “if a laurin (*sic*) fat or oil such as palm kernel oil is subjected to crushing, it will never become a slurry state.” However, a more mundane reason for this limitation is provided in (Sitzmann and Willner 1995), column 3, lines 27–33, which states that Wong Soon had already described the process for lauric oils in “A development approach to cocoa butter and cocoa butter replacers,” Kuala Lumpur, 1987.

Having convinced itself that palm kernel oil blocks could not be crushed to provide a pumpable slurry and could therefore not be processed in a similar process to the one disclosed in Kuwabara et al. (1991), Fuji Oil diluted the palm kernel oil with olein before the crystallization, as disclosed in Yoneda et al. (1997); this allowed the partially crystallized blocks to be crushed. In the US, this application led to two patents: US Patents 6,060,028 and 6,069,263, whereby the earlier patent is a division of the application that led to the later patent. Yet another patent applied for by Fuji Oil (Yoneda et al. 2000) discloses a dispenser to facilitate filling the trays with precooled molten fat; the application has been withdrawn, and there is no US equivalent.

Given the above Fuji Oil disclosures, it is not surprising that two of their patents (Kuwabara et al. 1991 and Yoneda et al. 2000)[10] were listed in the Search Report of an application filed by De Smet Engineering (Hendrix and Kellens 2003). This application discloses a fractionation process and an apparatus to perform this process, in which fat is crystallized in the form of blocks in a special apparatus that has a series of chambers that can be cooled. The apparatus can be opened like a plate and frame filter press so that the blocks can be discharged. Then they are crushed to form a slurry that is pumped to a filter press, where the olein is separated from the stearin filter cake. When communicating with the Examiner, we argued that we observed that surprisingly, and contrary to the teaching of Kuwabara et al. (1991), solidified palm kernel oil blocks could be crushed to a pumpable slurry and that we did not need to dilute the palm kernel oil with palm kernel olein as disclosed in Yoneda et al. (1997). Hence, patents were granted in Europe (DE, GB, and SE) and the US, and I gather that the apparatus (Statoliser®) is doing quite well.

In another patent application (Nezu et al. 2008), the stationary-phase transition is not from the liquid state to the solid state, but the other way around. It discloses a process in which a stearin filter cake is purified by sweating. I once visited a plant in Hamburg producing paraffin wax, and this plant operated a sweating section in which the paraffin that had solidified around a three-dimensional heat exchanger consisting of a network of narrow tubes was slowly heated by the same heat exchanger, causing liquid paraffin to drain away. This draining was by gravity, but in the application dealing with edible fats (Nezu et al. 2008), the heating operation is carried out in the filter press used to separate the olein from the stearin. Heating and continued pressing causes more olein to be collected so that a purer stearin is retained.

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[10] In the Search Report, this application is referred to as Taniguchi Atsushi et al. instead of Yoneda Shin et al.

12.3 Dry Fractionation with Agitated Crystallization

Fuji Oil is not only concerned with solvent fractionation and dry fractionation with stationary crystallization, but also with dry fractionation processes that employ an agitated crystallizer. The process disclosed in Kuwabara et al. (1993) is based on the finding that treating physically refined palm oil with activated carbon improves the crystallization process by generating large crystals that are readily separated from each other during the filtration stage. Consequently, the adsorbent treatment causes the olein yield to increase and the stearin IV to decrease. In Europe, the claims in the granted patent (EP 0 481 782 B1) are the same as in the application, but in the US, the main claim became more specific in that it specifies the physical refining as "comprising distallation (*sic*) at reduced pressure and at a temperature of at least 200°C."

The patent (Kuwabara et al. 1993) also applies to palm fractions such as, for instance, palm olein, which is the starting material in Example 2. The effect of the adsorbent is quite marked, and this made me wonder about a possible mechanism. In dry fractionation, the first crystallization tends to proceed through heterogeneous nucleation. Dirt particles act as nuclei and cause the crystallization to commence. These particles remain in the stearin and are no longer available to nucleate the crystallization of the olein. Consequently, the dry fractionation of this olein may take quite a bit longer than the first fractionation. One way to speed up the olein crystallization is by adding high-melting crystals such as trisaturates present in palm oil (Maes et al. 1995).[11] Another way might be to add an adsorbent since its removal by filtration will leave tiny adsorbent particles in the oil that can then act as nuclei.[12]

A later patent application (Kuwabara et al. 2007)[13] discloses a dry fractionation process to produce a fat with a high content of disaturated triglycerides. In this process, the stearin fraction (AF) resulting from the fractionation of a fat (A) containing both mono- and disaturated triglycerides is mixed with a fat that has a higher disaturated triglyceride content than fat (A). Such a fat can be obtained, for instance, by interesterifying the olein fraction (AL) resulting from the fractionation of fat (A) with a 1,3-specific enzyme. The patent reflects the interest Fuji Oil has in enzymatic interesterification.

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[11] This patent application was not pursued when the applicant (Vandemoortele) withdrew from its joint venture with Fuji Oil Co.

[12] It would be interesting to compare the crystallization behavior of an oil from which the adsorbent had been removed by the normal method of filtration with an oil that had passed through a membrane filter.

[13] Claims 5 of the application and of the granted patent (US Patent 7,727,569) read, "The fractionation method of claim 3, wherein the vegetable butter is palm oil, shea butter or illipe butter." However, neither claim 3 mentions any butter; the first time this starting material is mentioned is in claim 4. It is a minor point but, to me, illustrative of the time-saving use of the copy/paste subroutine.

Pall Corporation produces filters. It is therefore not surprising that it advocates the use of its filters in a dry fractionation process (Degen et al. 1995)[14] comprising feeding a suspension of crystals to a membrane surface of a dynamic microfilter whereby the suspension has imparted to it a secondary velocity component that is tangential to the membrane surface and that is independent of the feed rate of the suspension. By doing exactly the same, the bacterial count of the fat is also reduced, so this is also claimed without affecting the unity of invention.

When discussing (Kuwabara et al. 1991), I mentioned (Sitzmann and Willner, 1995) since the latter document devotes several columns to highlighting the shortcomings of the process disclosed in GB2 220 672, which is the UK equivalent of Kuwabara et al. (1991). Accordingly, the Krupp inventors Sitzmann and Willner (1995) disclosed a process in which the rate of cooling and the rate of agitation are carefully controlled in each of the consecutive stages of the crystallization steps. The examples reveal that the final step of the crystallization process is a stationary crystallization step. The patent was granted in the US, but in Europe, the application was withdrawn in 1998.

Another Krupp patent (Homann 1996) is concerned with a crystallization process carried out in a crystallizer in which the melt to be crystallized is virtually stagnant because the agitator assembly, which consists of a number of tubular heat-exchange elements, moves in this melt in such a way that these elements have the same relative velocity with respect to the melt. The process has also been described in the journal literature (Weber et al. 1998). The patent has been applied for only in Germany, where it was granted after slight amendment. As far as I am aware, the only crystallizer according to this process was built in Kenya and suffered from some mechanical teething troubles.

A somewhat similar crystallizer has been disclosed by Kellens and Hendrix (2007). The common feature is that the "various points of the agitator move at substantially the same linear speed," but there are also essential differences. The De Smet Mobuliser® is a rectangular vessel that can also contain stationary heat-exchange elements in between which the agitator assembly moves. To me, an interesting aspect of this crystallizer is that it has shown that the assumption that only temperature uniformity can assure a "good" crystallization is unfounded. Accordingly, it opens the way for a continuous dry fractionation process as specified in the last claim of the Mobuliser® patent. Another interesting aspect is that the absence of fast agitator movement may well suppress secondary nucleation, as a result of which the resulting crystals are very uniform in size.

A kind of continuous dry fractionation process is disclosed in a Loders Croklaan patent (Harris et al. 1999) in which a large crystallizer acts as a continuous stirred-tank reactor. The degree of crystallization within this crystallizer is specified in the

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[14] The US patent mentions Peter D. Degen as the inventor. However, all other 23 family members listed by INPADOC mention Peter J. Degen, where the J stands for John. All granted patents were allowed to lapse in 1998 or 1999 by non-payment of annuities or renewal fees.

main claim and should be at least half the degree of crystallization reached at equilibrium at the temperature of the crystallizer; in practice, it operates close to equilibrium. Its operation implies that molten fat is quench-cooled when fed into the crystallizer and mixed with its rather cold contents. The US patent (Harris et al. 1999) has twice the number of claims of the European equivalent (EP 0 776 357).

In another crystallizer without fast agitator movement (Kellens et al. 2009), the crystallizer does not even have an agitator. Heat transfer resulting from movement of the crystallizer contents along heat-exchange elements inside the crystallizer is realized by the intermittent application of pressure. According to the figures, the crystallizer can be a kind of U-tube fitted with internal cooling elements, whose contents are made to oscillate by periodically applying pressure. This can be by injecting an inert gas such as carbon dioxide or nitrogen or by the intermittent use of a fan.

Another patent originating from De Smet, albeit from a former employee, is (Athanassiadis 1993). This patent discloses a reaction vessel fitted with an agitator and heat-exchange coils that can be used for fractionation as well as hydrogenation. It has been summarized by Espacenet as follows:

> Method and installation to treat fat, particularly nutritional fat, such as crystallisation, hydrogenation and using at least one heat exchanger (9, 109), a determined quantity of fat being introduced into a confinement (1) comprising, on part of its height, a coaxial vertical central space (3) surrounded by a coaxial annular space (6), said quantity being selected such that said fat reaches a level (10) greater than that of the upper end (7) of said central space (3), said fat being placed in movement from one of the ends (7 or 8) of said central space to the other end (8 or respectively 7) of the central space (3) where the fat is distributed in the annular space (6) containing the heat exchanger (9,109) which extends through said annular space (6) over a significant part of the cross-section of said space, and the fat located in said annular space (6), being carried in the opposite direction to the flow of the fat in the central space (3), at least two levels . . . .

I included the above excerpt to illustrate why some people have given up consulting the patent literature; I do not blame them. Apart from stopping in mid-sentence, this claim is also incomprehensible, and the original French is not much better. What the claim attempts to specify is a vessel (“confinement”) that has a number of superimposed, horizontal, spirally wound heat exchangers, in between which the agitator blades force the vessel contents upward near the vessel wall and downward near the agitator axis. That way, there are a good heat exchange and a uniform temperature throughout the vessel. But the vessel has the serious disadvantage that when used as a crystallizer, it is difficult to empty the vessel because a fair amount of crystals stay put on top of the heat-exchange coils. Maintenance is also quite awkward with the agitator blades in between the coils.

The dry fractionation process got off the ground when Tirtiaux introduced the continuous vacuum belt filter (1976). It is therefore not surprising that his company continued to improve the process. One such improvement (Tirtiaux and Tan 2000) relates to a process in which the fat to be fractionated is divided into small beads that are cooled and allowed to crystallize by dispersing them in water. After several hours, the dispersion is fed to a membrane filter press that has been cooled to the temperature of the dispersion. First, the water is removed from the beads at low pressure; next, the beads are squeezed at high pressure. According to claim 5, the beads have a diameter between 1 and 3 mm. This means that they are much larger than the fat globules in cream that is being ripened before churning. Consequently, the likelihood that most beads contain at least one heterogeneous nucleus is quite high. This means that the crystallization process will take about the same time as observed during bulk crystallization. Patents were also granted in Europe and several other countries but allowed to lapse even before Fractionnement Tirtiaux went bankrupt in 2006.

Another patent application disclosing the use of direct water cooling is Deffense (1999).[15] In a continuous process, molten fat to be fractionated is entrained by a hydro-ejector (a kind of water aspirator), thereby producing a mixture of microcrystals that can subsequently be separated from the water and split into an olein and a stearin fraction in a membrane filter press. The example in the application describes the fractionation of palm kernel oil, but apparently (E. Deffense, personal communication, 1999) the process was difficult to reproduce; the application was withdrawn in 2001.

Wisconsin is a dairy state, and so it is not surprising that the fractionation of anhydrous milk fat has been studied at the University of Wisconsin. This study has resulted in a process (Hartel et al. 2000) and an apparatus (Hartel et al. 2002)[16] for the fractionation of various fats (milk fat, lard, tallow, and palm kernel oil) in which the fat is rapidly supercooled and subjected to shear forces to induce the formation of crystal nuclei whereupon the nuclei are allowed to grow under relatively static conditions. The patents reflect their university origin by including a long list of non-patent literature references and the results of a systematic investigation of the various process parameters.

Even so, I have my doubts about the basic assumptions made in the specification: They do not take into account the possibility/probability of heterogeneous nucleation and do not mention secondary nucleation either. I would not be surprised if the observations reported in the examples could be explained by assuming that some nuclei were formed heterogeneously during the supercooling and that these caused further nuclei to be formed by secondary nucleation caused by the relatively high shear forces.

Another patent disclosing the fractionation of anhydrous milk fat (Parmentier et al. 1998) employs a membrane that is made of stainless steel or Teflon®. Anhydrous milk fat with an SFI of 30 at 20°C can be split by tangential filtration into a retentate with an SFI of 33 and a permeate with an SFI of 26. This takes about 30 min. These fractions can be used to reconstitute a butter with slightly modified properties.

In 1989, Unilever was still actively involved in fractionation. So it is not surprising that an invention in this field (Keulemans and Van den Oever 1996) led to 11 applications.

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[15] Dr. Deffense worked for Fractionnement Tirtiaux until he started his own company: “Crystallisation & Degumming Sprl.”

[16] The front pages of both patents cite the same documents, so the printing error in US Patent No. 5,338,518, which should read 5,338,519, appears on both documents.

They disclose a countercurrent dry fractionation process in which a first fractionation step leads to a first olein and a first stearin; the first olein is fractionated to yield a second stearin and a second olein; and this second stearin is at least partially recycled to the first fractionation. This may sound complicated, but just imagine how confusing an explanation of the process variant comprising four steps would be. The claims also specify minimal separation efficiencies[17] of 0.4 and 0.5, which can be attained by using a membrane filter press.

Another Unilever patent (Arends et al. 2003) discloses a process in which the crystallizing melt is subjected to ultrasound in the absence of transient cavitation since this can lead to off-flavors:

> When investigating the deterioration effects of sonocrystallisation on triglyceride oil as a function of the sound intensity, frequency, temperature, presence of oxygen, addition of water, metal ion contamination and storage conditions, it has appeared that the major cause for off-flavor formation was the occurrence of cavitation during sonication.

Example 3 demonstrates the presence of sononucleation in the absence of transient cavitation, and Example 4 shows that a much higher separation efficiency (expressed as% solids in the filter cake) can be obtained as the result of sononucleation.

A milk fat substitute was disclosed by Huertas Amaya et al. (2009). It is based on palm oil and consists of a mixture two olein fractions. Accordingly, palm oil is fractionated to yield a first stearin and a first olein. Then the stearin is fractionated to yield hard, second stearin and a second olein fraction that is mixed with the first olein. The main claim of this application specifies the first step of the process as "fractionating the oil." Subsequent claims are mainly concerned with the pressures to be applied in the membrane filter press, and palm oil is only mentioned in claim 12. I would not be surprised if the Examiner were to insist that claims 1 and 12 be combined.

The English summary of a Japanese PCT application (Suganuma and Takaba 2010) discloses a process to remove trisaturated triglycerides (XXX) and disaturated diglycerides (XX) from a mixture that also contains disaturated triglycerides (XUX) to arrive at a product that is enriched in XUX-type triglycerides. The fractionation is carried out in the presence of a fatty acid lower alkyl ester that presumably acts as a kind of solvent that dilutes the olein retained in the filter cake and thus increases the olein yield.

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[17] On working my way through the specification, I did not come across a definition of this efficiency.

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Epilogue

When my wife worked her way through the last draft of my manuscript to polish my English and detect my typing errors,[1] she was originally a bit confused about the purpose of this monograph. After having read/corrected the first chapter, "Introducing the world of patents," she thought that I would concentrate on legal aspects of patents. Then I explained to her that I was not qualified to do so and that instead I was aiming to make people working in the edible oil industry more aware of what patents are and help them find out what they might have to offer. I also pointed out that this made sense now that patents are so much easier to get ahold of than in the past.

In my library, I have books on statistics (Davies 1967) and on Excel (Billo 1996) that have been written specifically for scientist/chemists. When introducing charts, the Excel book states

> Excel 5.0 provides a gallery of 15 chart types – bar charts, column charts line charts or pie charts among others. Since Excel originated as a financial tool, most of the chart types are useful for displaying financial and related information – a bar chart to show sales figures for each business quarter, a line chart to show stock values each day over a one month periods, etc. Only one kind of chart, the X–Y or scatter plot, is of general usefulness for displaying scientific data. It is the only one in which numerical values are used along both axes, p. 45.

Then the book focuses on the X-Y chart so that for a chemist, studying this book is a far more efficient way of familiarizing him- or herself with Excel than studying a more general book. I have also books on patents (Gordon and Cookfair 2000; Goldstein 2005) that have been written for scientists, and I studied them before starting with monograph, which is not about patents as such but about edible oil processing and the patent literature describing aspects of edible oil processing.

When reading what I had written, I realized that to understand some sections, you really needed to have access to the specification being discussed. These sections can

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[1] The first of my manuscripts she polished was my PhD thesis. She liked the work and since then, she has improved a vast number of manuscripts by a wide range of authors. Perhaps the most challenging manuscript I asked her to perfect was my draft translation from French into English of the first-ever book on lipid chemistry written by Chevreul in 1823. When translating, I concentrated on the chemistry and I left the English to my wife. She did a marvelous job and I thanked her as well as I could. Now I want to thank her again most warmly for her highly appreciated and invaluable contributions.

A.J. Dijkstra, *Edible Oil Processing from a Patent Perspective*,
DOI 10.1007/978-1-4614-3351-4,

be regarded as exercises and an opportunity for readers to visit the websites and follow the procedures I outlined. Hopefully, this will familiarize them to such an extent that when they are working in the laboratory or the plant, they will again visit those websites and profit from the information they gain and now know how to interpret.

Readers who have worked their way through this monograph and finally reached this last chapter may have been reminded of comments made by whoever edited their own manuscripts. That is understandable because I am active as an editor myself, but these readers should appreciate that I was not just trying to find fault but to provide examples of situations that could cause unforeseen problems. The way names are spelled or rather spelled incorrectly is an example of this: It complicates searches and may even disqualify their results.

Readers might also comment that the attention I give to a patent hardly bears any relation to its importance. Some patents I discuss in detail and other, perhaps more important ones, I just skim over. That is a fair comment. If a particular patent provided a good opportunity to illustrate a certain aspect of patents in general, I discussed it for that purpose, even if the patent had little technical importance. If subsequently, in the course of writing, a more important patent emerged that provided a similar opportunity, I did not cut the illustration I had already written and paste it onto the more important patent. Similarly, not all patents have been commented upon in the same degree of detail. That is because the kind of comments I made are very subjective. Some patents inspired me to comment upon them, whereas others did not.

Readers may also wonder why I inserted a number of autobiographical stories and remarks. Again, this is because science is subjective. My way of tackling a problem will differ from the way another scientist would tackle it. So providing some personal background may help to explain why I did things the way I did. That also holds for the slides I use in my presentations. I can illustrate that with the last two slides of my Bailey Award address. There is also an anecdote connected with these slides. After a Short Course, a registrant told me that she knew all about me since the colleague with whom she shared a room had copied the slide below and stuck it on the wall.

TAKE HOME MESSAGES

- Don't believe everything you read or people tell you
  - Besides, they contradict each other, so what to believe?[2]
- Question established "truths"; they can be myths
  - They may have originated as suggestions and then started to lead a life of their own
- Define the problem as concisely as possible
  - Then you are already halfway to the answer
- Think before attempting experimental verification
  - Thinking is cheap; you do it in bed or while driving to work
  - Laboratory work is expensive, especially when unnecessary
- Above all, enjoy. **CHEMISTRY IS FUN**
  - At least it should be and I hope to have shown that it can be.

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[2] Since I delivered the address in the US, I did not use the Bible as a prime example.

I have certainly enjoyed working on this monograph and I can only hope that my readers also enjoy reading it and that it serves the purpose of familiarizing them with the world of patents, or at least part of it.

And so we come to the final slide of every presentation I give:

DIXI

(I have spoken)

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[3] This book was published for ICI, and I suspect that the authors were ICI employees.

Author Index

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