

The Total Degumming Process

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A novel degumming process is described that is applicable to both undegummed and water-degummed oils. Such totally degummed oils have residual iron contents below 0.2 ppm Fe and residual phosphorus contents that average below 5 ppm P. Therefore, they can be physically refined to yield a stable refined oil while using the same level of bleaching earth commonly used for alkali refined oils prior to deodorization. They can also be alkali refined with reduced oil loss to yield a soapstock that only requires slight acidification for fatty acid recovery, and thus avoids the strongly polluting soap splitting process.

The total degumming process involves dispersing a non-toxic acid such as phosphoric acid or citric acid into the oil, allowing a contact time, and then mixing a base such as caustic soda or sodium silicate into the acid-in-oil emulsion. This keeps the degree of neutralization low enough to avoid forming soaps, because that would lead to increased oil loss. Subsequently, the oil is passed to a centrifugal separator where most of the gums are removed from the oil stream to yield a gum phase with minimal oil content. The oil stream is then passed to a second centrifugal separator to remove all remaining gums to yield a dilute gum phase which is recycled.

Washing and drying or in-line alkali refining complete the process. After the adoption of the total degumming process, in comparison with the classical alkali refining process, an overall yield improvement of approximately 0.5% has been realized. It did not matter whether the totally degummed oil was subsequently alkali refined, bleached and deodorized, or bleached and physically refined.

An important but over-emphasized aspect of edible oil refining is the removal of phosphatides from these oils. Some phosphatides can be removed by water-degumming, however, the remaining phosphatides, which Guillaumin *et al.* (1) have called "non-hydratable phosphatides" (NHP), require a chemical degumming process for their removal.

The effectiveness of such a chemical degumming process is often judged by the residual phosphorus content of the chemically degummed oil, which is commonly expressed as ppm phosphorus. This parameter is generally considered to be indicative of oil quality as well as its keepability, and suitability for physical refining (2).

In his article "Review of soybean oil reversion flavor," Smouse (3) lists a number of factors that could be responsible for flavor reversion but does not single out any particular oil constituent as its main cause. Grothues (4) is more definite in this respect by stating that "a good quality of oil requires the almost complete removal of the high phosphatide content. The stability and keeping quality of the finished oil is highly dependent on the level of oxidative iron."

We, the authors, have reason to believe that iron is the sole constituent responsible for flavor reversion. This would reduce the problem of producing a stable finished

product to developing a process for the effective removal of iron from the oil. We realize that copper is an even more powerful pro-oxidant than iron, but its presence can be minimized by suitable selection of construction materials, moreover, a process that effectively removes iron is highly likely to remove copper as well.

This raises the question of the forms in which iron is likely to be present in crude and water-degummed oils. As illustrated by the observation that agitating a soybean lecithin solution or dispersion with a magnetic stirrer causes some fine dust to be collected on this stirrer, some iron may be present as metal particles. Presumably, the hydrated phosphatides "sweep" the oil clean when they are centrifugally separated from the oil during water-degumming.

Water-degummed oil may, however, still exhibit an unacceptably high iron content, so that iron may well be present in another form, e.g., as ions bound to phosphatides in a way similar to that when Hvolby (5) found calcium and magnesium to be bound to phosphatides. Consequently, the problem of iron removal can be narrowed down to the development of a method of decomposing such iron/phosphatide complexes in such a way that the iron resulting from this decomposition step is converted into a form that can be effectively removed from the oil.

For this purpose, Hvolby (5) suggests the use of strong acids such as hydrochloric and citric acids, complexing agents such as EDTA, and precipitating agents such as citrates, etc. It is self-evident that the acid to be used to decompose the metal/phosphatide complex must be stronger than phosphatidic acid (PA) or lysophosphatidic acid (LPA) if the metal ions occur as salts of these acids, as suggested by Hvolby (5). Similarly, if a complexing or precipitation agent is used, this must have a stronger affinity to the metal ions than PA, LPA or the other phosphatides that are also known to form complexes with divalent metal ions, although the concentrations of the agents can also be manipulated to shift the dissociation and association equilibria in the direction required.

In this paper we will first describe the laboratory experiments that form the basis of the successful development of the total degumming process (6) and highlight those factors that have been found to be critical. Secondly, we will describe the development of an industrial process (7) based upon these laboratory findings with special emphasis on refining yields attainable as well as resulting oil quality. Finally, we will summarize our conclusions and discuss the potential advantages and benefits of the total degumming process as developed and practiced by our group.

LABORATORY EXPERIMENTS

All oil samples used in this study were taken from industrial production within the Vandemoortele Group and all reagents were analytical grade unless otherwise stated.

General procedure. After analysis for iron and phosphorus content by plasma emission spectroscopy (8), a sample of 300 g oil was heated in a 600 ml beaker on a hotplate with magnetic agitation to a temperature of

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THE TOTAL DEGUMMING PROCESS

usually 90°C and brought to the desired water content by the addition of demineralized water. Subsequently, the desired amount of acid solution was added and dispersed by homogenizing the oil/acid mixture for 30 seconds with an Ultra Turrax® at a speed of approximately 10,000 rpm. The emulsion obtained was agitated for a variable period of time (usually 3 min) with the magnetic stirrer.

Subsequently, a base or water was added to the emulsion, and after this had been thoroughly mixed through the emulsion with the magnetic stirrer, the mixture was transferred to two centrifuge tubes. It was then centrifuged for 30 min at 5,000 rpm, corresponding to 4,080 g in a pre-heated rotor to avoid the oil temperature dropping below 45°C.

After centrifuging the mixture, the top oil layers were decanted into a 600 ml beaker for washing with demineralized water. Washing involved reheating the oil to 90°C, adding the desired amount of water (usually 2 wt %), and dispersing the water with the magnetic stirrer. This washing water was then separated from the oil by centrifuge as described above.

Standard laboratory drying, bleaching, and deodorization techniques were used when required.

Importance of iron. Water-degummed soybean oil was heated to 75°C. An amount of 0.6 wt % water and 0.15 wt % phosphoric acid (89 wt %) were added and dispersed by homogenization. After 15 min of agitation by magnetic stirrer, 1.0 wt % demineralized water was added to the acid-in-water emulsion which was agitated for another 15 min. Subsequently, 1.0 wt % of magnesium oxide powder was added to the emulsion and allowed to react with the phosphoric acid for yet another 15 min, whereafter the mixture was separated by centrifugation. No washing step was included and the oil layer was bleached with 2.0 wt % bleaching earth at 140°C for 30 min and then physically refined. An aliquot of the same water-degummed oil was refined in the classical way (chemical neutralization, bleaching, and deodorization). Both samples were subjected to a shelf life test and were found to be equally good. The relevant analytical data are summarized in Table 1.

This experiment clearly demonstrates that a low residual phosphorus content is by no means a prerequisite for good keeping quality, provided the residual iron content of the fully refined oil is low (i.e., less than 0.2 ppm Fe).

The chemical reactions involved in the above experiment might well comprise: a decomposition of metal salts (including iron salts) of PA, LPA, and possibly other phosphatides by the stronger phosphoric acid with concomitant formation of metal phosphates (including iron

phosphate), PA and LPA; a reaction between the excess of magnesium oxide and the phosphoric acid to form magnesium phosphate; and a reaction between the magnesium oxide and PA and LPA to form oil-soluble (5) magnesium salts.

During the separation step, the excess of magnesium oxide, the metal phosphates including the iron phosphate, and the magnesium phosphate went along with the aqueous or heavy phase, whereas the oil-soluble magnesium (lyso)phosphatide remained in the oil phase, which therefore exhibited a high phosphorus content and a very low iron content.

It is well known that the addition of iron and copper salts to oils greatly diminishes their keepability. This is related to the inferred pro-oxidative effect of these multi-valent metals. Off-flavor components are oxidation products of some sort (9), so a role for iron as a cause of flavor reversion can easily be envisaged. For phosphatides, it is much more difficult to imagine such a catalytic role and, in fact, we have found them to be quite harmless in this respect.

Washing versus partial neutralization. A comparison was made between the effect of adding demineralized water to the acid emulsion and its partial neutralization with 2 vol % of dilute (5 wt %) caustic soda on residual phosphorus and iron contents of the oil after centrifugal separation. In this experiment the temperature was varied.

As indicated in Table 2, the use of water leads to much higher residual phosphorus levels than the use of dilute caustic soda. We suppose that this difference stems from a difference in degree of dissociation of (L)PA. If water is added, the diluted phosphoric acid still has a low pH, which causes the PA and LPA to be mainly undissociated and thus oil-soluble. Raising the pH by the addition of caustic converts the PA and LPA into their respective sodium salts, which are hydratable and therefore removed with the aqueous phase.

Iron is effectively removed because it is converted into insoluble iron phosphate, whether the phosphoric acid is merely diluted or partially neutralized. No clear explanation presents itself for the slightly but significantly lower residual iron contents observed at both temperatures for the partial neutralization. It may well be that the gum phase formed by the partial neutralization effectively sweeps the oil and assists in the removal of the last traces of iron phosphate particles. For this reason, partial neutralization has been adopted in subsequent experiments.

TABLE 1

Residual Phosphorus and Iron Contents After Neutralization with Magnesium oxide Versus Classical Refining

	Phosphorus (ppm)	Iron (ppm)
Water-degummed soybean oil	127	0.88
MgO-treated, before bleaching	84	0.04
MgO-treated, physically refined	73	0.14
Classically refined	1	0.20

TABLE 2

Residual Phosphorus and Iron Contents After Addition of Water and Caustic Soda

Temperature (°C)	Caustic/Water	Initial concentration		Concentration after degumming	
		Phosphorus (ppm)	Iron (ppm)	Phosphorus (ppm)	Iron (ppm)
90	Caustic	114	0.71	5.3	0.04
90	Water	150	1.02	63.5	0.12
75	Caustic	114	0.71	3.9	0.01
75	Water	150	1.02	34.8	0.12

Table 2 also shows that temperature has little, if any, effect. Apparently, the period of time allowed for the reaction between the acid and the iron salts already suffices at the lowest temperature used in this experiment.

Degree of neutralization. As a result of the above findings, the effect of the degree of neutralization upon residual phosphorus and iron contents was investigated using a sunflower oil (50.4 ppm P and 2.07 ppm Fe). In each experiment 0.6 wt % of water and 0.15 vol % phosphoric acid (89 wt %) were dispersed in the oil according to the general procedure described above, and the amount of dilute caustic soda was varied as indicated in Table 3. This table also lists the resulting degree of neutralization of the phosphoric acid, the resulting pH after partial neutralization, the residual phosphorus, and iron contents of the oil and its soap content after washing with 1 wt % of demineralized water.

As is to be expected, soaps are formed at a pH above six and the soap concentration increases with increasing pH. As will be shown below, this soap formation has an important effect upon the refining yield, and is preferably kept as low as possible. Little dependence of residual phosphorus and iron levels upon the degree of neutralization of the phosphoric acid is noted in these laboratory experiments.

Amount of acid and acid strength. In a recent article Liselott Nilsson-Johansson *et al.* (10) conclude that there is "no general relation between the concentration of phosphoric acid and the remaining phosphorus content in the oil." However, when we studied the effect of the amount of acid used and of its strength on a water-degummed, dried sunflower oil (50.4 ppmP, 2.07 ppm Fe) by varying the amounts of water and concentrated phosphoric acid added while keeping the degree of neutralization at 55.7% in each case, we observed a marked effect.

Table 4 clearly demonstrates that in the case of phosphoric acid effective iron removal requires a minimum acid strength of about 20 wt % but that this strength apparently has no upper limit. Acid amounts are apparently not critical either. Residual phosphorus levels are more difficult to interpret, however. Incomplete iron removal is caused by incomplete decomposition of (L)PA metal salts and thus leads to incomplete degumming because the remaining salts are oil-soluble. Consequently, the same minimum acid strength of about 20 wt % is required to obtain low residual phosphorus levels. It is clear from

TABLE 3

Residual Phosphorus and Iron Contents as Function of Degree of Neutralization

Amount of 7.5 wt % caustic (vol %)	% Acid neutralized	Phosphorus (ppm)	Iron (ppm)	Soap (ppm)	pH
0.8	22.3	11.3	0.16	0	2.0
1.0	27.9	3.9	0.12	0	2.4
1.2	33.4	7.0	0.15	0	3.4
1.4	39.1	4.5	0.11	0	5.4
1.6	44.6	3.3	0.13	0	6.0
1.8	50.2	7.9	0.13	25	6.8
2.0	55.7	7.2	0.10	16	7.2
2.2	61.3	12.8	0.24	95	7.9

Table 4 that high phosphoric acid strengths lead to high residual phosphorus levels, but it is doubtful whether the phosphorus measured stems from the phosphatides originally present in the oil or, as is more likely (T. K. Mag, private communication), from phosphorus containing reaction products formed by the action of the relatively large amounts of strong phosphoric acid on oil components.

Acid type. The literature lists many different acids used for the chemical degumming of triglyceride oils. Hvolby (5) suggests the use of hydrochloric and citric acids, Paul (11) uses strong mineral acids such as nitric, hydrochloric, phosphoric, and sulphuric acids, and Merat (12) has tried sulphuric acid but found it has disadvantages because of its reaction with triglycerides and prefers hydrochloric acid with calcium chloride, phosphoric, and boric acids. Finally, Ohlson *et al.* (13) studied oxalic acid as an alternative to phosphoric acid because of effluent implications.

For NHP decomposition, the acid used must be sufficiently strong, it should not react with oil components other than NHP, it must be non-toxic and, for process cost reasons, it must be as cheap as possible on an as-used basis, including corrosion aspects. Besides, its salts must not be oil-soluble.

A number of acids were studied in the laboratory using the general procedure and water-degummed sunflower oil as described above.

The data in Table 5 clearly show that acetic acid does not remove any iron, presumably because the iron acetates formed are oil-soluble. The rather high residual iron contents observed when hydrochloric and nitric acids are used may well have a similar cause. According to the data

TABLE 4

Residual Phosphorus and Iron Contents as Function of Amount and Strength of Acid Used

Water (wt %)	Phosphoric acid (vol %)	Acid concentration aqueous phase (wt %)	Phosphorus (ppm)	Iron (ppm)
5.0	0.10	3.0	19.6	1.00
2.5	0.10	5.8	11.6	0.94
2.0	0.10	7.2	11.9	0.54
1.5	0.10	9.3	8.2	0.38
1.2	0.10	11.3	6.6	0.33
0.6	0.05	11.3	11.5	0.33
0.9	0.10	14.5	8.1	0.25
0.6	0.10	20.1	6.6	0.19
0.6	0.15	27.1	4.7	0.10
0.3	0.10	32.8	10.3	0.16
0.6	0.20	32.8	6.5	0.25
0.6	0.25	37.5	3.0	0.17
0.6	0.30	41.3	2.5	0.12
0.6	0.35	45.1	2.0	0.12
0.6	0.40	47.9	3.9	0.12
0.6	0.50	52.6	6.1	0.12
0.6	0.60	56.6	7.9	0.12
0.6	0.80	62.3	6.6	0.12
0.6	0.90	64.3	36.0	0.07
0.6	1.00	66.3	48.4	0.18
0.6	1.50	72.3	59.1	0.14
0.6	2.00	76.0	36.7	0.17
—	0.60	89.0	134.0	0.07
—	0.10	89.0	70.7	0.53

THE TOTAL DEGUMMING PROCESS

in Table 5, sulphuric acid is not very suitable either and diluted sulphuric acid is quite corrosive and its reactivity towards triglyceride oils constitutes a further disadvantage. Phosphoric acid and sufficiently strong organic acids are apparently quite effective and quite acceptable.

Base type. In the experiment that demonstrated the importance of residual iron, magnesium oxide was used as a base to neutralize the acid used to decompose the iron salts present in the oil. Subsequent experiments reported have used caustic soda, and literature data show that Alexander (14) prefers an alkaline salt such as trisodium phosphate or sodium silicate, the latter of which is also said to be used in the HLS degumming process (15) as a "flocculating" agent.

When the experiment using magnesium oxide (see above) was repeated with 1 wt % of calcium carbonate instead of magnesium oxide, the soybean oil was found to contain 27.7 ppm P and 0.03 ppm Fe prior to bleaching and 8.3 ppm P and 0.06 ppm Fe after having been physically refined. Other bases were tested on the water-degummed sunflower oil used in previous experiments and into which 0.15 vol % of phosphoric acid had been dispersed.

As demonstrated by Table 6, iron removal is quite effective for all bases tested but residual phosphorus is significantly higher when bases derived from a divalent metal (i.e., calcium) are used than when sodium derived bases are used to partially neutralize the phosphoric acid. The most likely reason for this is that some of the (L)PA liberated by the phosphoric acid reacts with the calcium hydroxide to form calcium (lyso)phosphatide, which is oil-soluble.

TABLE 5

Residual Phosphorus and Iron Contents as Function of Acid Type

Acid type	Acid strength	Amount water (wt %)	Amount acid (vol %)	Phosphorus (ppm)	Iron (ppm)
Phosphoric	85 wt %	0.6	0.15	7.2	0.10
Hydrochloric	36 wt %	—	0.72	7.9	1.38
Acetic	99 wt %	0.33	0.42	29.5	2.00
Nitric	65 wt %	0.24	0.51	8.5	0.72
Sulphuric	96 wt %	0.55	0.20	16.2	0.31
Citric	640 g/l	—	0.72	3.5	0.07
Oxalic	600 g/l	—	0.75	8.6	0.13
Tartaric	1000 g/l	0.20	0.54	5.8	0.19

TABLE 6

Residual Phosphorus and Iron Contents as Function of Base Type

Base type	Concentration (wt %)	Amount added (vol %)	Phosphorus (ppm)	Iron (ppm)
Caustic soda	7.5	2	4.7	0.10
Soda ash	10.0	2	5.8	0.17
Lime	2	10	13.3	0.13
Water glass	18	2	5.7	0.13

INDUSTRIAL PRACTICE

Degree of acid dispersion. Early industrial trials were carried out by making use of an existing alkali refining line. The only modification provided at that time was a separate supply vessel for dilute (12 Bé) caustic soda to allow the line to be operated independently of the other neutralization lines.

The first experiments suffered from unexpected gum discharge problems, the gums were rather sticky and had an almost putty-like consistency. As a result, gums were insufficiently removed from the oil, and were only partially removed by the down-stream solid bowl disc centrifuges, which they rapidly fouled. This difficulty was overcome by increasing the degree of neutralization of the degumming acid, as a result of which some fatty acids were neutralized and some soaps were formed. These soaps combined with the gum phase and entrained appreciable amounts of triglyceride oil, causing the gum phase to become more fluid so that the self-cleaning disc centrifuge could achieve almost complete removal. On the other hand, the oil entrainment decreased the refining yield to values close to those observed with normal alkali refining.

However, degumming results (i.e., residual phosphorus and iron contents) were found to vary considerably. At first there seemed to be no apparent reason for this, but after a number of trials we came to suspect a variability in the degree of acid dispersion as a possible cause. This suspicion was based on microscopic examination of the acid-in-oil emulsions. However, microscopic examination is often difficult to interpret, and cannot be expressed quantitatively.

Quantitative description of the degree of dispersion became possible with the purchase of the Centrifugal Automatic Particle Analyzer (HORIBA CAPA 500), a photosedimentometer which uses Stokes' law for the calculation of particle size distributions, which makes this instrument ideal for emulsions with a transparent continuous phase.

Measurements on a sample of an acid-in-oil emulsion (0.35 wt % water, 0.15 vol % strong phosphoric acid) made with an Ultra Turrax[®] showed a number average diameter of 4.5 micron and a weight average diameter of 6.1 micron. These figures were considerably lower than those found for the rotary mixer in the industrial line. Given Mag *et al.*'s (16) claim of obtaining droplets below 10 micron by using a static mixer, the rotary mixer in the former neutralization line was replaced by a static mixer, but this led to even coarser dispersions as quantified by the CAPA 500. Finally, another mechanical dispersing device was adopted with satisfactory and reproducible results.

We think, and in this respect we agree with Mag *et al.* (16), that an average droplet size of about 10 micron is the maximum value for the reaction between the dispersed acid and the oil-soluble salts of (L)PA to be completed within the allotted period of time. However, we prefer to define this requirement in a way that is independent of the amount of aqueous acid used, and to express it as a minimum interfacial area to be calculated from the amount of acid dispersed and its particle size distribution, which should be at least 0.35 m²/100 g of dispersion.

For the variability of the performance of the rotary mixer in attaining a sufficiently large interfacial area, we

tend to blame variations in oil composition by assuming that some oils happen to contain more compounds with emulsifying properties than others and thus require less mechanical effort to be emulsified to the required degree of acid dispersion. The process invented by Alexander (14) for oils, in particular corn oil that are not yet water-degummed, may perhaps work because the hydratable phosphatides present in these oils facilitate a sufficient degree of dispersion.

Degree of neutralization. As indicated above, a high degree of neutralization was found to be necessary to allow the self-cleaning disc centrifuge to discharge the gum phase, but the resulting soap formation also leads to oil entrainment and thus a decreased yield of degummed oil. Adjusting the centrifuge operating parameters, decreasing its throughput, and testing other separation equipment such as decanters and various conveyors at a low degree of neutralization was tried. This led either to unacceptably high oil losses in the gum phase if complete removal of the gums was aimed at, or to incomplete

removal of gums if gums with a low oil content were the objective. Apparently, the gums contain a significant fraction that is not removed under those operating conditions in which the bulk of the gums are effectively discharged.

A solution to this problem has been found by the use of an additional centrifugal separator (Westfalia Separator KG, Oelde, West Germany) positioned downstream from the first one and adjusted so as to remove the gum fraction that is not removed by the first centrifugal separator (7). The gums removed by this second centrifugal separator were found to contain considerable amounts of triglyceride oils (more than 90% calculated on dry matter) and are therefore unacceptable as a refining loss. They have been recycled and, fortunately, no build-up of this gum fraction has been observed, despite the fact that during recycling all gums leaving the system have to be discharged by the first separator.

The flow diagram incorporating this second centrifugal separator is depicted in Figure 1. This figure indicates that the oil leaving the second centrifugal separator can

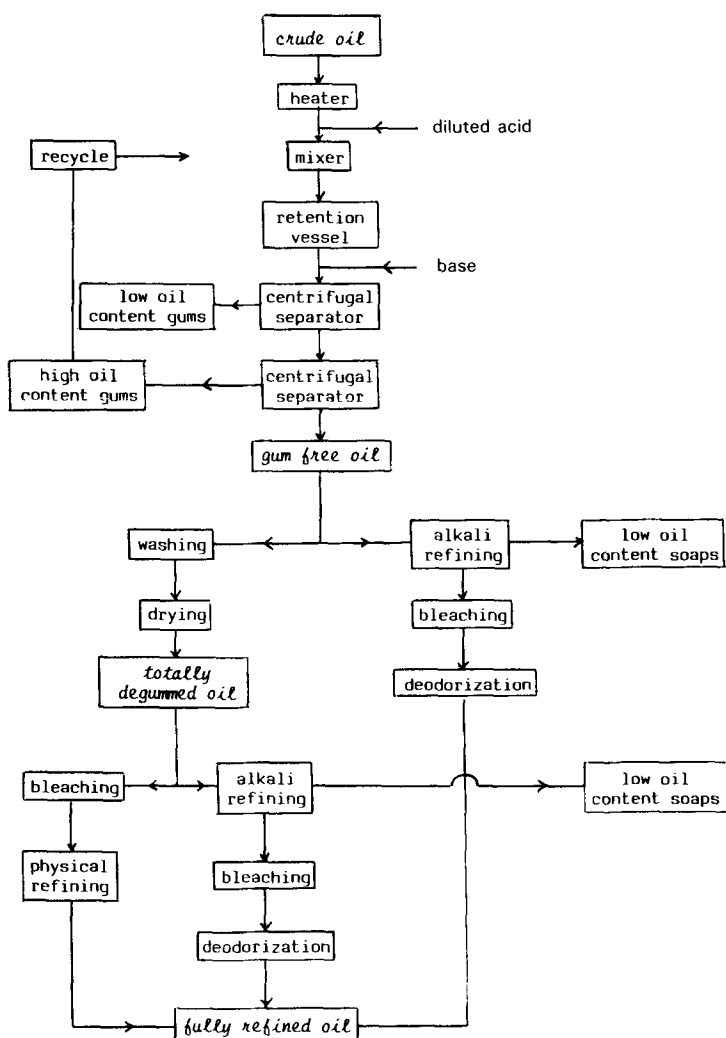


FIG. 1. Flow diagram for several possible refining routes, including the total degumming process.

THE TOTAL DEGUMMING PROCESS

either be washed with water to produce totally degummed oil for a commercial product, or it can be alkali refined with caustic soda to produce neutral oil. The advantage of this latter route is the improved yield over the classical alkali refining process which results from the fact that neutralizing almost phosphatide-free oil leads to very little oil entrainment with the soaps.

We also want to point out two disadvantages of using a second centrifugal separator. Firstly, the net throughput of the line is reduced by 10–15% because of the recycling of the gum phase, and secondly, it requires additional investment.

Quality of totally degummed oil. An industrial trial was carried out using water-degummed soybean oil with 109 ppm P, 0.1 wt % water and 0.52% FFA. In this oil, 0.20 vol % of technical phosphoric acid (80%) was dispersed together with 0.20 wt % of water. The acid was neutralized with 12 Bé caustic soda to a neutralization degree that was varied during the trial between 40 and 60% and washed with water until an amount of 400 tons had been collected. The properties of this totally degummed oil are given in Table 7, column A.

This lot was split into two parts, one part being alkali refined to a free fatty acid content of 0.03%, bleached and deodorized, and the other part being just bleached and physically refined. Bleaching conditions were identical in both cases and employed 0.44 wt % bleaching earth (Tonsil ACCFF) at the same temperature (approximately 100°C). This amount of bleaching earth is considerably lower than the amounts recommended for the super degumming process (17). The continuous deodorization process was carried out at a throughput of 25 tons/hr whereas in the physical refining process the equipment and the operating conditions used were the same but throughput was reduced to 18 tons/hr. Subsequent physical refining trials have indicated that a reduction in throughput of 10% also leads to a fully acceptable refined oil quality, but this observation may be limited to the equipment used within the Vandemoortele Group. Samples were taken at two- or four-hour intervals and analyzed to arrive at the data summarized in Table 7.

TABLE 7

Properties of Totally Degummed Soybean Oils

	A	B	C	D	E	F
Free fatty acid (%)	0.38	0.03	0.38	0.05	0.02	0.02
Phosphorus content (ppm)	4.0	1.3	1.0	0.9	1.3	0.8
Iron content (ppm)	0.07	0.03	0.05	0.03	0.04	0.06
Extinction 268 nm	0.22	0.14	1.22	1.29	1.20	1.24
Extinction 232 nm	2.0	2.1	2.0	2.2	4.4	4.5
Anisidine value	0.5	1.0	1.7	2.2	1.2	1.5
Peroxide value					0.3	0.1
Color (4 1/4")					0.7/4	0.6/4
Taste						
Fresh					8.5/10	8.5/10
After 1 week					8.5/10	8.5/10
After 2 weeks					8.0/10	8.0/10
After 4 weeks					8.0/10	8.0/10

A, Totally degummed oil after water washing; B, Oil A—after alkali refining; C, Oil A—after bleaching; D, Oil B—after bleaching; E, Oil C—after physical refining; F, Oil D—after deodorization.

Table 7 illustrates that soybean oil can be physically refined to yield an oil that is equally stable as an oil that had been chemically neutralized, while using the same amount of bleaching earth. This means that oil loss during bleaching is the same in both cases.

In the case of sunflower oil, it has been noted that totally degummed sunflower oil as such, or after chemical neutralization, exhibits improved filtration characteristics during the subsequent winterization process. This phenomenon was first noticed in the laboratory after a method for the quantification of filterability had been developed (18) and subsequently confirmed by industrial trials. The reason for the improved filterability of totally degummed sunflower oil is not clear but we assume that during the total degumming process other, non-triglyceridic components than phosphatides are removed at the same time as the phosphatides.

In the case of rapeseed oil, total degumming removes some of the components that inactivate nickel-based hydrogenation catalysts, and it was found possible to use less catalyst and/or use this more often. In addition, it has also been found that it was possible to hydrogenate totally degummed oils prior to their being neutralized.

Crude oil quality. Before adopting the total degumming process on a routine basis, a great number of trials were carried out on crude oils of as widely varying quality as available and, in fact, this work is still in progress. It has been noted that all soybean oils with an extinction of a 1% solution at 232 nm below 2.8 could be totally degummed to a sufficiently low iron content (i.e., less than 0.2 ppm Fe) and to a phosphorus content below 5.0 ppm P. Some oils with a higher extinction could be totally degummed to a phosphorus content below 5.0 ppm and some could not, but all oils with a higher extinction could be degummed to a residual iron content below 0.2 ppm Fe, and therefore had good keeping quality. Besides, a simple process step has been developed to further reduce the phosphorus content of totally degummed oils to levels below 5.0 ppm P if the customer happens to insist on this level being reached.

Oil yield on total degumming. The many industrial trials carried out have also been used to quantify and optimize refining yield. On the basis of these trials (after omitting what were obviously rogue values), we calculated an average overall refining yield and compared this with the overall refining yield obtained from monthly production statistics for classical alkali refining. A difference of 0.5% in favor of the total degumming process was observed for soybean oil. For other oils, this increase in refining yield looks to be somewhat higher, but sufficient data are not yet available for significant quantification.

Attempts have also been made to predict the loss on total degumming as a function of phosphatide content and water content of the oil to be totally degummed. This has been done both by analyzing the gums discharged by the centrifugal separator and by overall loss determinations. Although these analyses highlighted the low oil content of the gums in comparison with their phosphatide content, no exact prediction has resulted so far. Apparently, some crude oil constituents which have escaped analysis so far and happen to occur in variable amounts affect the yield during total degumming by decreasing it by a small but significant and unpredictable amount.

For soybean oil, the overall refining yield does not

depend upon the subsequent treatment of the totally degummed oil. Treatments compared are the bleaching/physical refining process and the alkali neutralization/bleaching/deodorization process. This may look surprising, but analysis of the soaps resulting from the alkali neutralization of totally degummed oil support the observation that their oil content is very low indeed (about 10%) and thus not that different from the oil content of the distillate resulting from physical refining. The low oil content and the total absence of phosphatides in this soapstock also imply that its splitting is a very simple process indeed: mere acidification suffices and the resulting effluent therefore has a relatively low BOD and mineral content.

It is clear from the above data that the improved refining yield stems from the fact that the gums have as low an oil content as possible and that the subsequent (and separate) removal of free fatty acids also allows a minimal oil loss. The total degumming process avoids the simultaneous removal of free phosphatides and free fatty acids and thus leads to improved refining yields.

RESULTS AND DISCUSSION

Several conclusions have already been indicated in the description of the laboratory experiments and the industrial trials. These and other conclusions can be summarized as follows: residual iron content determines finished oil quality and the amenability of totally degummed oil to being physically refined; a low residual phosphorus content is indicative of a low residual iron content but a high residual phosphorus content does not necessarily imply an unacceptably high iron content and thus poor keeping quality; iron salts present in crude oil can be effectively decomposed by dispersing a sufficiently strong acid in the oil, provided that this dispersion has an interfacial area of at least $0.35 \text{ m}^2/100 \text{ g}$ dispersion and that the iron thus liberated can be effectively removed from the oil, if the acid used forms a precipitate (phosphoric acid), or a complex (citric acid, etc.) with the iron ions; acetic acid and, to a lesser extent, hydrochloric and nitric acids are, although sufficiently strong, not suitable because of the oil-solubility of their iron salts. In practice, 0.10–0.20 vol % of strong (80%) phosphoric acid diluted to an acid strength of 20–60 wt %, and a reaction time of about 2 min are found to be effective, given the required degree of dispersion. Adding water to the acid-in-oil emulsion and separating the aqueous phase from the oil phase and washing the oil phase with water effectively removes iron to below 0.2 ppm Fe, but does not lead to low residual phosphorus levels, presumably because of the oil-solubility of undissociated (lyso)phosphatidic acid. Adding a base to the acid-in-oil emulsion can lead to low residual phosphorus levels of 5–10 ppm P after separation of the aqueous phase and the oil phase, and water-washing the oil phase. Many different bases are suitable for this purpose, e.g., caustic soda, sodium carbonate, sodium silicate. If calcium hydroxide or calcium carbonate are used for the neutralization of the acid, incomplete phosphatide removal is observed, because (L)PA reacts with these bases to form oil-soluble calcium complexes. In practice, no retention time is necessary after the addition of the base to the acid-in-oil emulsion. The temperature during the

degumming process is not very critical and a range of 70–110°C is permitted.

During the partial neutralization of the degumming acid, soap formation is preferably avoided by limiting the degree of neutralization of phosphoric acid to 50%, because at higher degrees of neutralization serious oil losses are unavoidable. At this low degree of neutralization, the gums have an oil content (about the same weight as the phosphatides removed or slightly less) that is so low as to cause the gums to be very sticky and putty-like in consistency. Commonly used centrifugal separators turn out to be incapable of achieving a complete separation if they are adjusted so as to minimize the oil content of the gums. They then leave a fraction of the gums in the clarified oil. This gum fraction can be effectively removed from the clarified oil stream by using a second centrifugal separator leading to gum free oil which after having been washed with water, yields totally degummed oil with a low content of both iron and phosphorus. The gum phase from this second centrifugal separator can be recycled into the oil stream entering the first separator without creating a build-up of this gum fraction.

A refining yield improvement of 0.5% has been observed when comparing alkali refining of soybean oil with totally degumming this oil and following this process by washing/bleaching/physical refining, or by washing/alkali refining/bleaching/deodorization, or by alkali refining/bleaching/deodorization. This yield improvement is more or less independent of the route taken, because the amount of bleaching earth required prior to physical refining is the same as prior to deodorization and because the triglyceride oil content of the soapstock resulting from alkali refining is about the same as the oil content of the fatty acids resulting from physical refining.

For oils other than soybean oil, the yield improvement resulting from the adoption of the total degumming process looks like being somewhat higher than the 0.5% mentioned earlier. The total degumming process requires some additional investment in metering pumps, dispersion devices, and centrifugal separators. But although these investments will vary according to actual situations, they are highly likely to yield a high return because of the ensuing refining yield improvement. Return on capital is even higher if effluent aspects are taken into account, but the magnitude of this increase is highly site-dependent. Totally degummed sunflower oil has significantly improved filtration characteristics during winterization. Totally degummed rapeseed oil may inactivate hydrogenation catalysts less rapidly.

The question to be discussed now is which parts of the total degumming process described above are of interest in what circumstances and to which crusher/refiner. In this respect, it must first of all be noted that the total degumming process has many facets. For example, it allows a refiner to use his existing alkali refining plant with a minimum of alterations requiring investment. He can use his first separator to remove most of the gums with minimal oil losses, then use a second centrifugal separator to fully remove residual gums and then use subsequent separators for the alkali refining of the degummed oil and thus reap the benefit of a soapstock with low phosphatide content and low oil content, which soapstock can be processed by simple neutralization. This will improve his refining yield by an estimated 0.5% and

THE TOTAL DEGUMMING PROCESS

greatly alleviate his effluent problems resulting from soapstock splitting.

The refiner may also totally degum oil on his existing alkali refining line after having slightly modified this line and subsequently physically refine the totally degummed oil. This will hardly lead to a better overall yield compared to alkali refining totally degummed oil, but leads to even fewer effluent problems, because the only effluent resulting from this situation is the washing water from the total degumming process, which only contains the acid not removed with the gums.

A crusher, on the other hand, may want to sell totally degummed oil to refiners who want to limit their process to just physical refining, or to refiners who face an effluent problem with their soapstock splitting. Further, as suggested by Alexander (14) the crusher can also blend the gums resulting from his total degumming operation with the meal originating from his crushing operation and sell these for meal price. Refiners may well sell the gums resulting from the total degumming process to the feed industry and thus significantly increase the return on their total degumming investment.

We consider the total degumming process a worthwhile improvement over existing processes in that it allows crushers and refiners to improve their yield and cut down on costs involved in soapstock splitting and effluent treatment, and provides them with a profitable investment opportunity. Besides, we hope to have contributed to an increased insight into oil refining mechanisms by exposing a number of myths.

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