Boiler horsepower	1.67 HP/ton
Water consumption	7.3 ℓ/min/ton not including cooling water make-up
Hexane consumption	3-8 ℓ/ton is manufacturer's guarantee, depending on plant capacity.

These figures are calculated for plants with evaporation economizing and dehulling of beans for production of high-protein meal.

IMPORTANCE OF SOYBEAN OIL IN TODAY'S VEGETABLE OIL CONSUMPTION

According to industry records published by the American Soybean Association, soybeans constitute 53% of the total oilseeds in the world. Soybeans are so important that they outrank their nearest competitor, cottonseed, by a margin of 3.7-1. The total estimated production of oilseeds for the year 1980 is 181,812,000 metric tons.

The expected production of soybeans for this year is 97,596,000 tons. According to the same sources, soybean oil is used in the United States for 80% of salad oils, for 78% of margarines, 75% of cooking oils and 59% of manufactured shortenings.

Modern Innovations at Soybean Extraction Plants

Because gums in crude soybean oil tend to collect at the bottom of storage tanks, partly through the action of residual moisture in the oil, many plants degum the oil at the extraction site. This operation allows the plant to handle degummed oil exclusively, as the degumming operation is incorporated into the extraction area.

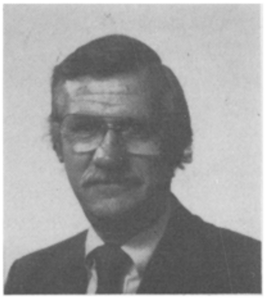
As a result, many plants have installed facilities to dehydrate and blend gums to convert them into various types of finished lecithin, thus making available several more finished products at the extraction location.

With the increased interest in the use of soybean meal for direct human consumption, a modern innovation in extraction plants is the installation and operation of special desolventizers with a wide range of protein solubilities for the production of soybean flours. These flours also are ground to several different particle sizes in response to a growing market demand.

These new developments in solvent extraction plants for soybeans, along with the need for increased efficiency and improved product quality, are demanding a higher technical level for personnel operating and directing these plants as the extraction operation becomes more complex.

REFERENCES

1. Bauer, S.T., in "Soybeans and Soybean Products," Interscience Publishers, Inc., New York, NY, 1950.
2. Hayward, J.W., in "Soybeans and Soybean Products,"
3. List, G.R., et al., JAOCS 54:8.
4. Soyanoticias, American Soybean Association, Año XI, No. 117, June 23, 1980.
5. Greenbank, R.G., "Conversions," (pamphlet) The French Oil Mill Machinery Co., Piqua, OH.
6. Hutchins, R.P., JAOCS 53:281.



Degumming, Refining and Bleaching Soybean Oil

L.H. WIEDERMANN, Consultant, 1828 Lincoln St., Des Plaines, IL 60018

ABSTRACT

This subject deals with the removal of the fat-soluble impurities from crude soybean oil. These impurities may be present in true solution or in a colloidal state; their effective removal is necessary to achieve quality standards for end-use products. The processing step options for the removal of these impurities in any given situation are easily defined; the conditions and practices used, however, are the primary concern of this paper. International trading of soybean oil mandates the degumming step. The increased use of import/export soybean oil increases the importance of this processing practice. Pretreatment and effective contact time are the critical issues. Refining, as a specific process, deals primarily with free fatty acid removal, with or without simultaneous degumming as a single-step operation. State-of-the-art wet, chemical refining practices are described, and the current limitations and future opportunities for the physical refining of soybean oil are discussed. The importance of the bleaching step cannot be overstated and it should be noted that color reduction is only coincidentally achieved. The primary function of the bleaching process is to remove oxidative breakdown products, and the degree or level of treatment should be consistent with that objective. Underbleaching and thermal decolorization (deodorization) of soybean oil are misguided practices. Once "cleaned-up" through adequate bleaching, an oil should be guarded against thermal/oxidative abuse.

INTRODUCTION

The emphasis of our subject needs to be turned around and our objective stated as the removal of fat-soluble impurities present in crude soybean oil. These impurities may be present in true solution or in colloidal suspension, and their effective removal is absolutely necessary to achieve the finished soybean oil quality standards for flavor, appearance and stability required by end-use product applications. The unit processes usually associated with this task are degumming or desliming, refining, both chemical and physical, and adsorptive bleaching (1-6).

The soluble impurities in crude soybean oil are identified as gums or sludge which consist of phospholipids, the crude lecithins and metal complexes (notably those of iron, calcium and magnesium), free fatty acids (FFA), peroxides and their breakdown products, and pigments. These impurities are present in crude soybean oil as a natural consequence of extraction. Table I cites typical levels for these impurities in crude soybean oil.

Gums and metal complexes are removed by degumming or chemical refining; free fatty acids are removed by either chemical or physical refining, and oxidation products and pigments are removed in the bleaching step which will also clean up any traces of gums and soaps from refining. Contrary to some views, no significant oxidative breakdown products are removed by deodorization; their only opportunity for removal is in the bleaching step.

The task for the removal of these impurities is defined by crude oil quality which, in turn, is supplemented by oilseed quality, i.e., the quality of the soybeans from which the crude oil is extracted. In starting with degummed oil, the task is more or less complicated by the conditions of that initial treatment.

Table II cites some of the potential abuses to both beans and oil that can directly affect crude oil quality and complicate our unit process practices–weed-seed contamination, use of immature or field-damaged beans, extraction of splits developed during handling and of improperly stored beans, poor conditioning of flakes for extraction, overheating during solvent stripping, and just the age of the beans and crude or degummed oil.

All of these potentially contribute to increased levels of soluble impurities and, in some cases, make them more difficult to remove, most notably the nonhydratable phospholipids and metal complexes.

Trading rules do not provide a basis to measure or assess crude oil quality in terms that totally describe these impurities. Therefore, we should be aware of the potential effects that these abuses have on our processing practices and the quality of oil we expect to get from such processing. Because the basis for predictable practice is limited, it is important that we adopt the philosophy of MINIMUM TREATMENT PRACTICES to ensure maximum finished oil quality in spite of crude oil quality condition, a philosophy that also provides for ADJUSTED TREATMENT PRACTICES to ensure uniform finished oil quality from varying crude oil sources. This is the underlying theme for our discussion.

The sequence or order of removal of the soluble impurities is important and can be classified in terms of conventional practices which are: refine and bleach; or degum, refine and bleach; or innovative alternatives such as degum, bleach and deodorize.

If the oil processor is not interested in crude lecithin recovery or preparing oil for export, the degumming function is combined with centrifugal alkali refining in a single step; the water-washed and dried oil is then bleached.

TABLE I

Typical Range of Soluble Impurities in Crude Soybean Oil (7)

Phosphatides[a]	1.5-2.5%
Phosphorous[b]	600-800 ppm
Unsaponifiable matter	1.6%
Sterols	0.33%
Tocopherols	0.15%
Hydrocarbons	0.014%
Free fatty acids	0.3-0.8%
Trace metals	
Iron[c]	1-3 ppm
Copper	0.03 ppm
Calcium[d] Magnesium[d]	80-200 ppm

[a] Calculated basis phosphorus X factor of 30 (8).

[b] From normal (undamaged) beans (10).

[c] Could be 3X in oil from damaged beans (10).

[d] Will vary considerably (9,11,28) depending on quality conditions.

As an option, crude oil can be degummed prior to alkali refining. All oils for export are traded as degummed rather than crude oil. The pragmatic need for degumming is to avoid the potential for gum precipitation in crudes due to moisture contamination. Degumming, worldwide, is an important processing step. The refining procedures and conditions, with the exception of treat level, is the same for both crude and degummed oils.

Innovative processing schemes are important for their potential to eliminate or reduce a by-product's impact on pollution, to provide opportunities to upgrade by-products and to yield greater process efficiencies. These approaches would eliminate alkali refining and substitute physical refining or deodorization for removal of FFA in a purer, up-graded state (20). The success of this approach depends on effective degumming (21-23). Additional innovations involve modifications of the bleaching step such as alumina (24) or carbon column substitution, or combining the degumming and bleaching steps as recommended by "clay-heat" processing (25).

CONVENTIONAL PRACTICES

Conventional degumming and alkali refining processes are shown schematically in Figure 1. The process starts with a crude oil supply. Feedstock uniformity is essential for steady-state operation, and efficient centrifugal separation depends on maintaining a steady-state condition. For this reason, agitated day tanks are used to provide homogenous batches of crude oil sufficient for 12 to 24-hr continuous runs. Several day tanks may be necessary to provide time to prepare and test the oil and select appropriate refining

TABLE II

Crude Oil Quality, Affect of Abuse Characteristics

Abuse characteristics	Increase in:[a]	Reference
Weed seed	4,6	12
Immature beans	6	13
Field-damaged beans	1,2,3,5	14,15
Splits (loading/transport/unloading)	1,2,3	13,16,17
Bean storage (time/temp/humidity)	1,2,3	14,15,18
Conditioning beans for extraction	1,2,4,5	19
Solvent-stripping oil (overheating)	2,4	33
Oil from stripper (overheating)	2	33
Crude oil storage (time/temp)	3,4	33

[a] 1 = total gums/phosphatides; 2 = nonhydratable phosphatides; 3 = free fatty acids; 4 = oxidation products; 5 = iron/metal content; 6 = pigments.

conditions.

In degumming, the phosphatides are conditioned with phosphoric acid and hydrated with water. The resulting insoluble, hydrated gum is separated as a sludge by centrifugal action and, when dried, is a crude lecithin supply (26). The degummed oil can be dried and pumped to degummed oil storage or it can proceed to the refining step.

In the refining step, either the degummed oil or the phosphoric acid conditioned crude oil is continuously mixed with a proportioned stream of dilute caustic soda, NaOH solution and, after mixing, the emulsion is heated to effect a break. The resulting soapstock is then continuously separated from the neutral oil in the primary centrifuge. The refined oil is mixed with hot, soft water and again centrifugally separated to remove residual soaps. The water-washed, refined oil, containing traces of moisture, is then passed through a continuous vacuum dryer and is ready for bleaching.

The basic reactions involved in these processes are shown in Figure 2. Soybean gums are a complicated mixture of lipid structures containing a phosphorus moiety. These structures can be complexed with carbohydrates or metals. The three types designated here do not attempt to define specific structures, but represent generalized compositional classifications related to reaction conditions required to remove them from the crude oil.

One fraction of phospholipids, sometimes identified as α-lipoids, reacts easily with water and readily precipitates as oil-insoluble hydrates. The β-lipoids and metal-complexed fraction are nonwater precipitable without some pretreatment. These were earlier identified as non- or difficult-hydratable phospholipids that build up as a result of oil or bean abuse. Normally, they can be expected to be ca. 10% of the total gum content; however, they could easily be 2-3 times that level. Strong alkali, caustic soda (not carbonate) will attack the β-lipoids, and they are best removed in the refining step (27).

The metal complexes require phosphoric acid pretreatment or "conditioning" for their removal in either the degumming or the refining step. Iron soaps are prooxidants and calcium and magnesium result in nonwashable soaps (28).

The FFA react with alkali to form oil-insoluble soaps. The critical steps to effect these reactions and separate their reaction products are: (a) crude oil feed, (b) selection of reactants' (c) proportioning, (d) mixing, (e) contact time, (f) heating, (g) separation/centrifugation, and (h) monitor/evaluation. A general discussion of these steps will be helpful before we identify the specific conditions for each processing step.

We have already indicated the need for a uniform feedstock and its importance to steady-state operations.

The selection of reactants requires a consideration for kind and amount of water, mineral acid and alkali: the use of soft water in the water washing stage and for dilution of concentrated alkali, and the concentration and percentage excess of alkali to be used.

Proportioning or controlled delivery of reactants into the oil stream should be uniform and nonpulsating in order to maintain steady-state conditions.

Mixing, contact time and heating are particularly specific for soft oils such as soybean oil. The key phrase here is effective contact time: intimate mixing of oil with reactants and maintaining that mix. Soybean oil, unlike hard oils or high-acid oils, requires longer effective mixing times for contact with phosphoric acid, particularly in degumming, and for contact with alkali in the refining sequence. Versatile operations, handling both hard and soft oils, and attempting to use Short-Mix equipment without adequate

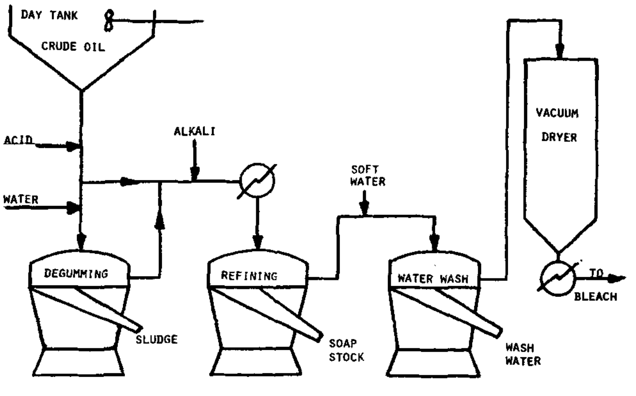


FIG. 1. Conventional degumming and alkali refining processes.

modifications to ensure effective contact time, cannot produce optimal quality soybean oils.

Preheating and postheating conditions, before and after contact with reactant, are especially specific for the refining step, which depends on thermal shock to effect a break in the emulsion for separation of the soapstock from neutral oil.

High-speed, centrifugal separation operates on a difference in densities between two immiscible substances. Even under optimal conditions, complete separation of two phases can never be achieved. The efficiencies for both yield and quality resulting from separation in the primary centrifuges depend on steady-state operations in the centrifuge and the separation of a heavy phase with the least amount of entrained oil. This separation is accomplished by allowing a small quantity of the soapstock phase to pass along with the refined oil for subsequent removal in the water washing stage (1). Low-loss oils, such as degummed soybean oil, should be separated by centrifuges equipped with bowl flush units to dilute their characteristically more viscous soap phase (2,29).

In-line control systems, in conjunction with analytical testing, are used to evaluate the crude and refined oils, monitor refining efficiencies, and indicate when and what adjustments are necessary for steps a-h (1,30,31).

The working conditions for batch-continuous and continuous degumming are suggested in Table III. The level of water used is ca. 2%; excess water will result in excessive oil losses at the centrifuge. In batch treatment, the mixing time requirement is longer because of poorer contact conditions. The batch procedure is the usual practice for lecithin production, and phosphoric acid pretreatment is not used because it darkens the crude lecithins, a practice which potentially produces poorer quality degummed oils.

The level of acid treatment varies basis crude oil quality and is usually made at a lower temperature. Ideally, the degumming step would utilize acid pretreatment in the

1. PHOSPHOLIPIDS (α- LIPOIDS) $\xrightarrow{\text{WATER}}$ HYDRATED GUMS

2. PHOSPHOLIPIDS (β- LIPOIDS) $\xrightarrow[\text{ALKALI}]{\text{ACID}}$ HYDRATED GUMS

3. METAL/PHOSPHOLIPID COMPLEX $\xrightarrow{\text{ACID}}$ HYDRATED Fe-GUMS

CALCIUM/MAGNESIUM $\xrightarrow{\text{PHOSPHATE}}$ INSOLUBLE PHOSPHATES

4. FREE FATTY ACIDS ———— ALKALI→SOAPS

FIG. 2. Reactions involved in degumming and alkali refining.

TABLE III

Working Conditions for Batch-Continuous and Continuous Degumming

- Batch-continuous
  - 2% water in mix tank
  - 30 min-1 hr @ 60-70 C (140-160 F)
  - Centrifuge
- Continuous
  - Preheat oil 60-70 C (140-160 F)
  - Add 2% water
  - 10-15 min mix-residence time
  - Centrifuge
- Acid pretreatment
  - 0.05-0.2%, 75% phosphoric acid
  - Mix 4 hr in day tank @ 33 C (90 F)
  - 1 min @ 70-90 C (160-195 F)/Super Mix

day tank followed by continuous water hydration. If the crude is to be continuously treated with acid, the contact time is a function of temperature and mixing efficiency. Phosphoric acid is more soluble in oil at higher temperatures. Again, effective mixing time is stressed.

The quality control tool for degumming is measurement of phosphorus and iron contents. An analysis of crudes sets the treatment level and an analysis of the degummed oil indicates how well the job was done. The past and current degummed oil quality concerns are based primarily on phosphorous content without an appreciation for the potential detrimental effects of iron soaps. If iron soaps are strong prooxidants, then degummed or export oils are particularly vulnerable to oxidative deterioration if their iron contents are not minimized.

A comparison of the phosphorous and iron contents of some crude oils was made by List et al. (32). There was absolutely no correlation between the two, even for this small, limited, regional sampling. However, when the same oils were water-degummed, the iron-phosphorous correlation assumed some significance (Fig. 3), suggesting that the better the degumming, the lower the iron content. Nevertheless, in the absence of an acid pretreatment, the iron levels of 0.4-0.5 ppm are still high. This also begs the question of whether the NSPA Standard for 200 ppm phosphorous in degummed oils is low enough. It appears that, based on the subsequent discussion, a phosphorous level of ca. 50 ppm or less is necessary (and achievable) to ensure a reasonable degummed oil quality. This is based to a large extent on phosphorous level relationships to residual iron contents.

The effect of phosphoric acid pretreatment on residual phosphorous and iron contents as a result of processing is illustrated by Figure 4. The iron content of the pretreated oil after degumming is significantly lowered. Even subsequent bleaching had little lowering effect on the iron content of non-pretreated, degummed oil. Alkali refining did, however, lower its iron content, but not to the same extent as in the pretreated oil.

It is difficult to conclude, in absolute terms, what the minimum allowable iron content should be. The question of trace metals concerns its qualitative nature as well as its quantitative aspects; it is a question of the metal's ability to do damage. A prudent conclusion, however, suggests that phosphoric acid pretreatment represents a MINIMUM TREATMENT practice.

The literature suggests that phosphoric acid appears to be markedly specific for this purpose, providing oil quality improvements in preference to such other pretreatment agents as tartaric acid, citric acid, acetic anhydride, oxalic acid and other mineral acids such as hydrochloric and sulfuric acids (28). Recent work with oxalic acid suggests that it is as effective as phosphoric acid for removal of phosphorous (35); however, no data for corresponding residual iron is reported.

The self-restricting water degumming conditions for degummed soybean oil for lecithin quality potentially jeopardize the quality of the resulting degummed oil. Based on an estimated 100,000 metric ton/year world demand for lecithin (26), we can conservatively estimate that as much as 20% of the world's supply of processed soybean oil could be in this classification. This estimate assumes that ca. 75% of the world's supply comes from soybean oil.

In refining soybean oil, the reduction in phosphorous content is determined largely by the amount of water present in the caustic solution, i.e., its concentration. Figure 5 shows that for a constant and comparatively small excess of alkali, e.g., 0.1%, there is less phosphorous remaining in the oil, as more dilute lye is used. Higher excesses remove more phosphorous, but the differences in the degree of removal become rather small. This is true because, for lyes of constant strength, more water as well as more caustic are provided by the greater excess, and this additional water removes more phosphorous. Soybean oil, therefore, is best refined with dilute caustic solutions; however, if they become too dilute, difficult emulsion separation characteristics develop. For this reason, caustic solution concentrations of 16-18 Baume are recommended as optimal (1,2).

The working conditions for continuous alkali refining

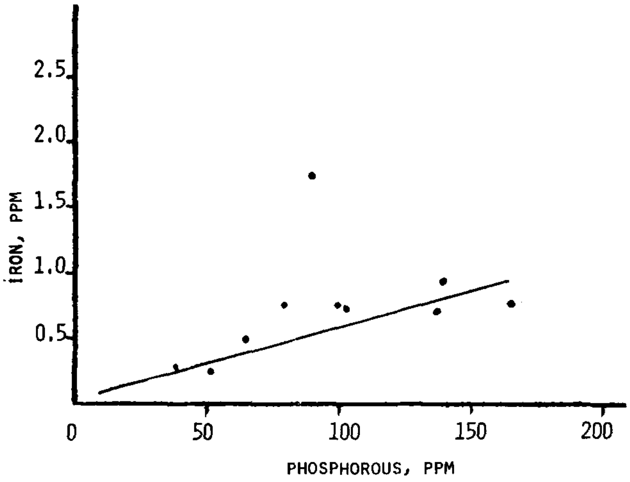


FIG. 3. Phosphorous vs iron content in degummed oils; correlation coefficient = 0.8715 (9 pt) and 0.5380 (10 pt).

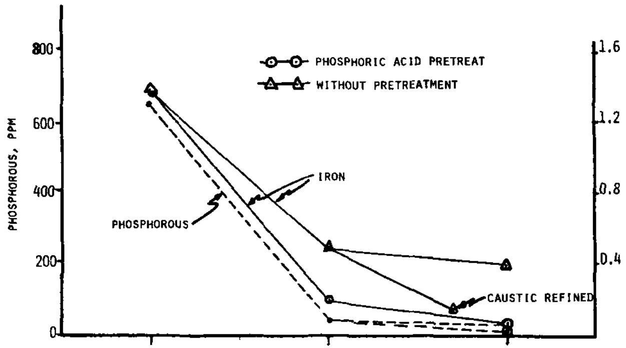


FIG. 4. Effect of phosphoric acid pretreatment on iron and phosphorous content of soybean oil during processing (23).

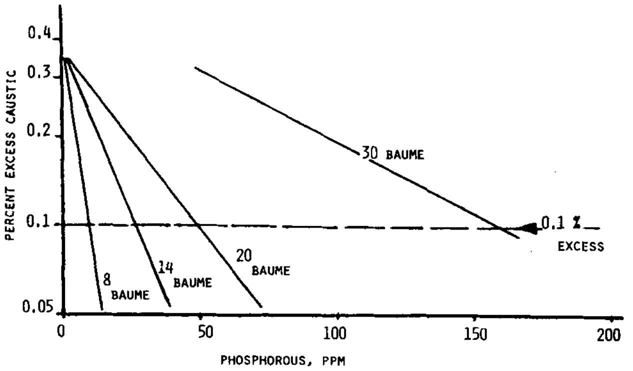


FIG. 5. Phosphorous content vs strength and quantity of lye used for refining (34).

are suggested in Table IV. The amount of alkali is based on the theoretical amount needed to neutralize FFA. This amount should also compensate for phosphoric acid added in any pretreatment step. The excess over theoretical amount to be used is less for degummed oil than for nondegummed oil.

The caustic solution is proportionately added into the warm (not hot) oil stream with good mixing, and this intimate contact with oil is maintained for at least 5-10 min in mixing vessels. Dwell mixers provide dwell time; they must also provide effective contact of oil with caustic solution.

The emulsion is then thermally shocked by heating to ca. 75 C to break out the soapstock which is then centrifugally separated from the neutral oil. Soapstocks from degummed oil are somewhat more viscous than those from nondegummed oil and need some bowl-wash assistance in the centrifuge for efficient separation. Oils that have been pretreated with phosphoric acid have poorer emulsion stability and separate more efficiently (36).

The recommended conditions for water washing are shown in Table V. One must use softened water to avoid formation of insoluble or unwashable soaps (37). Sodium soaps from the refining step are readily washable and easily removed from the neutral oil with either a single or double water washing operation. If one wash is good, two washes are twice as good.

Two things that water washing will not do, however, are removing phosphatides left in the oil from the refining stage or removing unwashable soaps. With respect to removing unwashable soaps, soybean oil is variable and this is related to the calcium and magnesium contents of the crude oils. As suggested earlier, calcium and magnesium are removed by phosphoric acid pretreatment. If not, some will carry through into the neutralized oil as reported by Braae et al. (28). Residual soap in refined oil without treatment was 2,700 ppm and after water washing, 1,600 ppm. Pretreatment with 0.2% H_3PO_4 reduced the soap content in refined oil to 800 ppm and after water washing to 60 ppm. There was an obvious reduction in residual soap content associated with pretreatment.

TABLE IV

Working Conditions for Continuous Alkali, Wet Refining

- Proportion 16-18 Baume Caustic plus
  0.12-0.15 for crude oil
  0.10-0.12 for degummed oil
- To cold, 33 C (90 F) oil
- 5-10 min contact time
- Heat to 75 C (165 F)
- Centrifuge

TABLE V

Water Washing Conditions (1,2)

Single
- 15% Hot (93 C/200 F), soft water
- Mix
- Centrifuge

Double
- Twice with 10% hot/softened water

The water-washed, refined oil is continuously dried through a vacuum dryer and is now ready for bleaching.

Absorptive bleaching, as an art and a science, is somewhat simpler than refining. Although its reactions are neither less complicated nor better understood, its practice is more straightforward and easier to effect. However, its real purpose is not always appreciated. Experimental evidence indicates that, in addition to physical adsorption, which we usually associate with color body removal, processes involving chemisorption and subsequent chemical reaction proceed on the surface of activated clays (37). Figure 6 illustrates one such concept that is extremely important to oil quality: the decomposition and dehydration, or pseudoneutralization of peroxides (38,39).

The primary function, therefore, of the bleaching process is to remove peroxides and secondary oxidation products. Secondarily, the process cleans up traces of soap and phosphatides from the refining step and removes pigments. The process does effect significant color reduction. Color reduction of soybean oil is, however, only coincidentally achieved in the bleaching process and in the deodorization step. Table VI indicates the typical range of colors that can be expected from each processing step.

Color standards can be used to monitor these processes, but only after appropriate empirical relationships have been established. An underbleached oil, e.g., to a 4-Red color, easily heat bleaches in a deodorizer to under a 1-Red color, but produces an oil of substantially lower quality. Good oils have good colors, but not all good colors represent good oils.

The basic kinds of materials used in edible oil bleaching are neutral clays, activated earths, synthetic silicates and carbon black. For soybean oil processing we are concerned only with acid-activated bleaching earths. The others are ineffectual.

Activated earths are made from certain bentonites, specifically Montmorillonite, which has little natural

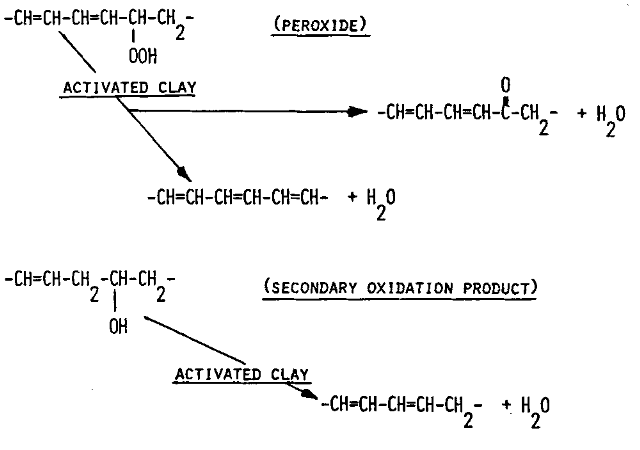


FIG. 6. Decomposition and dehydration or pseudo-neutralization of peroxides and secondary oxidation products (38,39).

bleaching power because the aluminum ions in its structure are relatively intact. The natural clay is treated with sulfuric acid and, in its activation, the aluminum is replaced with hydrogen ions. The excess mineral acid is removed by water washing, then the activated earth is dried and milled (40, 41).

The important characteristics of activated bleaching clays are: total acidity, pH, moisture, apparent bulk density, effective surface area, and oil retention. Acidity is classified as both bound and free, measurable as titratable acidity and as pH. Total acidity or "boil-out" acidity is determined on a water extract of the clay and pH is determined on a slurry of the clay in water (42). These are excellent quality control standards for monitoring bleaching clay supplies.

Bleaching power appears to be more a function of a clay's bound acidity; therefore, those clays with high total acidity and a reasonable level of free acidity are preferred. If an activated clay is washed completely free of residual acid, its bleaching power is drastically reduced.

Bleaching clays normally contain 10-18% moisture. Moisture plays an integral role in the physical structure of the clay. If the clay is completely dried prior to use, its internal structure collapses, resulting in reduced bleaching power because of decreased surface area.

The apparent bulk density, weight/unit volume, depends on the amount of void space in the clay's structure; the more void space, the lower the density, and the more oil is retained in the spent or used earth. Acid activation proportionately lowers the natural clay's density and increases its oil retention (43,44). However, because significantly less amounts of the more activated clays are usually required, the net oil loss is usually less for the more effective bleaching earths.

A comparison of several clays available in the world market are shown in Table VII, and are listed in descending order of bleaching effectiveness. These data also illustrate a laboratory bleach test to evaluate the comparative effectiveness of the clays. Peroxide reduction, starting with a refined oil with a 4.0 peroxide value is the judgment criterion; color is satisfactory in each instance.

Table VIII compares two activated clays in a plant test situation starting with the same refined oil source. This is an atmospheric bleach using 0.5% clay; the press capacity was such that six consecutive batches could be pressed out before cleaning.

The superiority of the 105-product over the 54-product is dramatic in terms of peroxide reduction. Peroxide value is measured in the oil directly off the press; it determines dosage or level of treatment and is a simple and convenient quality control or in-process control tool with which to monitor the operation. The continued or progressive reduction in peroxide value through the batches is due to "press effects," a benefit derived from build-up of clay in the press with each succeeding batch.

Important bleaching criteria or considerations include: activated earth, dosage, temperature, time, mixing, and atmospheric vs vacuum (41-45). We have already discussed clay choice.

The dosage or amount of activated clay to be used should be the minimum amount needed to effect removal of impurities as measured by peroxide reduction with zero peroxide as a goal. Normally, this requires 0.3-0.5% clay on a weight basis and will be dependent on the quality of the oil to the bleachers and press effect opportunities. Clay usage should follow the ADJUSTED TREATMENT philosophy which is guided by equal-performance and not equal-amount practices.

Adding clay to hot oil reduces its adsorptive capacity because the moisture in the clay is driven off too rapidly, causing collapse of the clay's lattice structure which, in turn, reduces its effective surface area before the clay has had an opportunity to do its work.

Under atmospheric bleaching conditions, the clay should be added to dry, refined oil at 80 C (180 F), rapidly brought up in temperature to 100-110 C (220-230 F), and held at that temperature for sufficient time to drive off moisture and effect maximal bleach. There is no need to exceed this top temperature.

Time is not as critical as top temperature. Usually 15-20 min contact time is adequate to drive off moisture and complete the reaction. Prudent practices suggest that presses be available to press out the oil after this minimal contact time.

Agitation in the bleaching vessel should be sufficient to achieve good contact of clay with the oil without incorporation of air.

Vacuum bleaching, batch or continuous, is somewhat more effective than atmospheric bleaching. It can use less clay, quantity not quality, operate at lower top temperatures, and minimize oxidation by reducing exposure to air and providing an opportunity to cool the oil before return-

TABLE VI

Typical Lovibond Colors

From refining		7-8 R
From bleaching		2-2.5 R
From deodorization		0.4-0.8 R
4-5 R	Heat Bleach	<1.0 R

TABLE VII

Comparison of Some Activated Bleaching Clays Available in the World Market

	Total acidity			Bleach[b]	
	(%)	KOH[a]	pH	PV[c]	Color
Filtrol 105	0.42	4.8	3.0	0	1.3 R
Vega Plus	0.39	4.5	3.0	0.2	1.3 R
Optimum X-FF	0.32	3.7	3.5	1.2	1.4 R
Filtrol 54	0.15	1.7	3.5	1.2	1.4 R
Optimum FF	0.04	0.4	3.0	1.0	2.0 R
Refined oil	—	—	—	4.0	5.2 R

[a] mg KOH/g.

[b] Laboratory bleach, 1% earth; Lovibond Index.

[c] Peroxide value.

TABLE VIII

Plant Bleaching Test: Comparison of Two Activated Bleaching Earths[a]

	Batch #	PV[b]	Color[c]
Refined oil to bleacher		2.2	7.9 R
Filtrol 54	1	1.7	3.5 R
0.15% Acidity	2	1.3	3.2 R
3.5 pH	4	1.5	3.3 R
	6	0.5	3.1 R
Filtrol 105	1	0.4	2.0 R
0.42% Acidity	2	0.0	2.0 R
3.0 pH	4	0.0	1.8 R

[a] 0.5% earth added @ 180 F; temperature raised to 220 F; held 20 min and pressed out; atmospheric conditions; 6-batch capacity press.

[b] Peroxide value.

[c] Lovibond Red Index.

ing it to atmospheric conditions. Although vacuum bleaching practices are preferred, atmospheric bleaching can produce high quality bleached oils.

Once "cleaned-up" through adequate bleaching, an oil should be guarded against thermal and oxidative abuses with the judicious use of heat exchangers and bottom filling ~~tank~~ practices (46).

It is well known that refiners will, from time to time, attempt to correct high peroxide value oils with redeodorization. The thermal decomposition of peroxides is complete, but the rate of peroxide formation in the oil during subsequent storage is increased and the flavor stability of the finished oil compromised. Properly handled, the oil would have been rebleached before redeodorization. Peroxides should not be allowed to build up in oils prior to heat treatments encountered during hydrogenation and deodorization.

INNOVATIVE ALTERNATIVES

Two alternative processing approaches currently in limited commercial practice are miscella refining and the Zenith process.

At facilities with an existing solvent extraction system, miscella, or solvent refining may be advantageous. The miscella can be treated to condition the gum prior to caustic addition; the alkaline emulsion is heated to 65 C, cooled to 45 C and centrifuged to separate refined miscella and soapstock. Compared to conventional refining, the process can result in lower refining losses and eliminates ~~water washing and~~ vacuum drying (47,48).

The Zenith process is a continuous process that includes a bleaching step. After treatment with concentrated phosphoric acid and centrifugal separation of hydrated gums, the oil is neutralized as droplets, rising by gravity through a lye column. The alkali concentration is weak and keeps the soaps in solution. This eliminates the formation of emulsions and saponification of neutral oil. This process eliminates water washing prior to bleaching and claims improved yields and excellent oil quality (49).

Without significant added capital investments and utilizing equipment that is basically already in-house, the most obvious innovative processing alternative is the elimination of alkali refining and its attendant soap stock acidulation by (a) pretreating, (b) degumming, (c) water washing, (d) bleaching, and (e) deodorizing.

It was earlier indicated that this requires an efficient degumming operation and that FFA are removed by physical refining in the deodorization step. Also suggested was that water degumming alone will not remove the nonhydratable phosphatides normally removed by alkali refining, and that water degumming and alkali refining did not provide for adequate or consistent removal of metals, particularly iron. Pretreatment with phosphoric acid prior to degumming for removal of both metals and nonhydratable phosphatides is, therefore, essential to this scheme, and a water washing step may be useful to counter the less than 100% separation encountered in initial centrifugation.

The question of allowable residual phosphorous (and iron) levels in the degummed and bleached oil for this approach is unresolved at this time. Pragmatically, it will have to be qualified in absolute terms; in theory, it will be dependent on its qualitative aspects, i.e., the form in which it is present in the oil, rather than its actual level (quantitative aspects). This phosphorous level could be as high as 10 ppm or as low as less than 5 ppm; nevertheless, an appreciation of this "allowable" level will be necessary for the consistent production of good quality finished oils by this approach.

For those operations currently refining crude oils, the primary centrifuges would be dedicated to a degumming operation. The bleaching operation is like that described earlier and the only remaining question is the capacity of in-house deodorizers to handle the small, but consistent, level of FFA in crude soybean oil, both in terms of collection and corrosion.

The most interesting innovative approach in recent years is the substitution of a bleaching alternative to this scheme, i.e., one that recycles the adsorbent and eliminates oil losses and the need to dispose of spent earth.

The basic engineering for this pulse-bed activated carbon column process has been used for some time for the purification of corn syrups (50). Activated carbons have been greatly improved and preliminary work with soybean oil is promising, but the approach needs confirmation.

As we look to innovative alternatives, it will be absolutely necessary for us to appreciate minimal and adjusted treatment practices required to consistently achieve minimal residual levels of soluble impurities in finished oils, levels that are consistent with finished oil quality objectives. The key to the success of these alternative approaches is this consistency.

ACKNOWLEDGMENT

The author acknowledges liberal use of referenced texts in preparation of this manuscript. It was not possible to identify the source of each "original" thought for such a generalized and often reviewed subject; the writer has only put this subject in a contemporary context.

REFERENCES

1. Sullivan, F.E., JAOCS 45:5164A (1968).
2. Carr, R.A., Ibid. 53:347 (1976).
3. Braae, B., Ibid. 53:353 (1976).
4. Carr, R.A., Ibid. 55:765 (1978).
5. Andersen, A.J.C., "Refining of Oils and Fats for Edible Purposes," Pergamon Press, 1962.
6. "Bailey's Industrial Oil and Fat Products," Third Edition, edited by D. Swern, Interscience Publishers, 1964, Chapter 16, p. 719.
7. "Handbook of Soy Oil Processing and Utilization," edited by D.R. Erickson, E.H. Pryde, O.L. Brekke, T.A. Mounts and R.A. Falb, published jointly by American Soybean Association, St. Louis, MO, and American Oil Chemists' Society Champaign, IL, 1980, p. 14.
8. "Official and Tentative Methods of the American Oil Chemists' Society," Third Edition, AOCS, Champaign, IL, 1975, Method Cc 13c-50.
9. Letan, A., and A. Yaron, JAOCS 49:702 (1972).
10. Evans, C.D., G.R. List, R.E. Beal and L.T. Black, Ibid. 51:444 (1974).
11. Hvolby, A., Ibid. 48:503 (1971).
12. List, G.R., G.F. Spencer and W.H. Hunt, Ibid. 56:706 (1979).
13. Gustafson, E.H., Ibid. 55:751 (1978).
14. Robertson, J.A., Ibid. 50:443 (1973).
15. List, G.R., C.D. Evans, K. Warner, R.F. Beal, W.F. Kwolek, L.T. Black and K.J. Moulton, Ibid. 54:8 (1977).
16. Velasco, J., and A.A. Abdul-Baki, Ibid. 56:970 (1979).
17. Mounts, T.L., G.R. List and A.J. Heakin, Ibid. 56:883 (1979).
18. Chapman, G.W., Jr., and J.A. Robertson, Ibid. 54:195 (1977).
19. Becker, W., Ibid. 55:754 (1978).
20. Sullivan, F.E., Ibid. 53:358 (1976).
21. Gutfinger, T., Ibid. 55:856 (1978).
22. List, G.R., T.L. Mounts, K. Warner, and A.J. Heakin, Ibid. 55:277 (1978).
23. List, G.R., T.L. Mounts and A.J. Heakin, Ibid. 55:280 (1978).
24. Crossley, A., A.C. Davies and J.H. Pierce, Ibid. 39:165 (1962).
25. Mag, T.K., Ibid. 50:251 (1973).
26. Van Nieuwehuyzen, W., Ibid. 53:424 (1976).
27. British Patent 1,001,159 (1965).
28. Braae, B., U. Brimberg and M. Nyman, JAOCS 34:293 (1957).
29. Klein, K., and L.S. Crauer, Ibid. 51:368 (1974).
30. Crauer, L.S., and F.E. Sullivan, Ibid. 38:172 (1961).
31. "Digital Refining Loss Monitor," Elliott Automation Co., Cincinnati, OH.
32. List, G.R., C.D. Evans, L.T. Black and T.L. Mounts, JAOCS

55:275 (1978).
33. Ohlson, J.S.R., Ibid. 53:299 (1976).
34. Beal, R.E., E.B. Lancaster and O.L. Brekke, Ibid. 33:619 (1956).
35. Ohlson, R., and S. Svensson, Ibid. 53:8 (1976).
36. Braae, B., Chem. Ind. 1958:1152.
37. Khoo, L.E., F. Morsingh and K.Y. Liew, JAOCS 56:672 (1979).
38. Ney, K.H., Fette Seifen Anstrichm. 66:512 (1964).
39. Pardun, H., et al. Ibid. 70:531 (1978).
40. Kogler, H.P., Ibid. 65:834 (1963).
41. Richardson, L.L., JAOCS 55:777 (1978).
42. Rich, A.D., Ibid. 44:298A (1967).
43. Rich, A.D., Ibid. 37:305 (1960).
44. Hasnuddin Siddiqui, M.K., Ibid. 45:885 (1968).
45. Rich, A.D., Ibid. 41:315 (1964).
46. Burkhalter, J.P., Ibid. 53:332 (1976).
47. Thomas, R., and J. Ridlehuber, Ibid. 45:254A (1968).
48. Bahret, E., "Developments to Date in Soybean Oil Miscella Refining," short course for oil mill operators, Texas A&M University, April 1967.
49. Hoffmann, Y., JAOCS 50:260A (1973).
50. Bulletin 19-23, Pittsburgh Activated Carbon, Div. of Calgon Corp. Pittsburgh, PA.

Hydrogenation

R.R. ALLEN, W.L. Clayton Research Center, Anderson Clayton Foods,
3333 N. Central Expressway, Richardson, TX 75080
Presented by Anthony H. Chen.

ABSTRACT

Hydrogenation of vegetable oils as it is practiced today is described as theory and process. Double bonds in the fatty acid portions of the oils are saturated with hydrogen and rearranged to produce many isomers during the process.

Hydrogenation of vegetable oils is a rather recent development that has had a great impact on the agriculture and food industry throughout the world. After discovery by Normann in 1902, the liquid phase hydrogenation was brought to the United States about 1920. It has grown into the large industry of today. Although the basic process has been used for many years and billions of pounds of products have been prepared, the reaction has never been fully understood; it is extremely complicated, occurring only when the liquid vegetable oil, hydrogen gas and solid catalyst are brought together under the correct set of conditions.

Batch hydrogenators are rather simple equipment, consisting of a tank, a pump to get the oil and catalyst in and out, a perforated pipe to put the hydrogen into the tank as small bubbles, and an agitator. A typical hydrogenator is shown in Figure 1. This shows the bubbles of hydrogen rising through the oil-catalyst mixture and collecting in the headspace while the agitator circulates the gas bubbles so the gas will dissolve in the oil, go to the catalyst and meet the unsaturated vegetable oil. Thus, the 3 reactants are brought together.

To understand this, an individual catalyst particle and an individual bubble of hydrogen are shown in Figure 2. The gas A is being dissolved in the oil both from the headspace and the bubble, migrating to the solid catalyst particle where it reacts with the double bond B to form the product C, releasing some heat to the surrounding oil. However, it really is not so simple, as shown in Figure 3. To reach the surrounding oil, the hydrogen must migrate first through the stagnant layer surrounding the bubble then into the oil so that the concentration is lowered. When hydrogen reaches the catalyst particle, a layer must also be penetrated; again, this resistance lowers the total concentration of hydrogen. Also, the unsaturated oil must penetrate the barrier to reach the catalyst so that the concentration of unsaturated oil is also decreased. Only with very vigorous agitation will these resistances be overcome and then only the kinetics, temperature and pressure will control the speed of hydrogenation. Most commercial hydrogenators are "underagitated," meaning the rate of reaction is controlled by the rate of migration of the hydrogen and double bonds to the catalyst surface. Although temperature and pressure affect the kinetics, the main effect of these reaction parameters is on the rate of migration of the hydrogen.

When the hydrogen and double bond meet at the catalyst surface, a reaction occurs. Unfortunately, we do not know what actually happens on the surface or in the catalyst pores because our knowledge is limited about the catalyst surface or pores. In fact, we know more about the

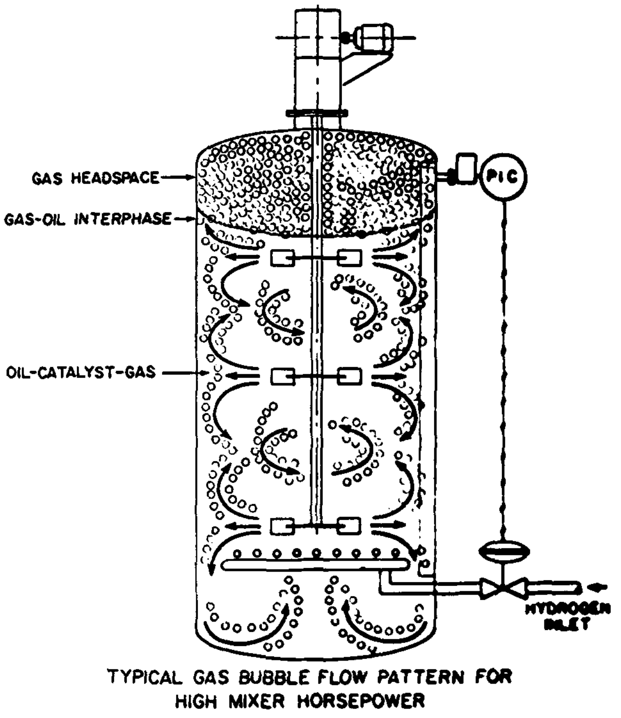


FIG. 1. Batch hydrogenator.