Cattle usually will consume the darker grades of fat if it is used with molasses, which has a strong odor of its own that cattle seem to like.

The rapid expansion in the use of fat in feeds has not been without certain difficulties. The feed industry had to learn how to handle fat. They had to learn how to store it, heat it, and mix it into feed during the cold winter months when other feed ingredients were cold and the fat had a tendency to form fat balls. Since large tonnages of feed are pelleted, the industry had to learn how to make a hard pellet containing fat.

It was mentioned earlier that fat in the feed resulted in a lowered power requirement in pelleting but that some lubricating action in the pellet mill resulted in a softer pellet if more than 5% fat was used. The feed industry soon learned that better pellets could be made by first mixing about 3% fat into the feed, running it through the pellet mill, and then spraying hot fat onto the pellets as they emerged from the mill. It was found that high levels of fat could be incorporated into pellets by allowing them to absorb hot fat in this way and the pellets remained hard.

The industry also learned that as the energy content of the feed was increased, the protein and vitamin content had to be readjusted to take advantage of the increased energy level. Most of the problems of handling fat in the feed industry had been solved by the latter part of 1957 when a strange new disease of chickens appeared in certain areas of the country, the causative factor of which appeared to be in some of the fat that had been used. The material causing the trouble, later called the chick edema factor, was found in certain fat-like materials that had somehow found their way into the fat. The factor has been isolated, but as yet we do not know what it is. We think that we know enough about it to prevent its recurrence, and the chick disease caused by it has not reappeared for quite some time.

The increase in the use of fat in feeds since 1957 indicates that the feed industry has confidence in the product and all indications are that fat usage in feeds will continue to grow.

Refining, Bleaching, Stabilization, Deodorization, and Plasticization of Fats, Oils, and Shortening

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ALTHOUGH the final products from our industry may be only the words, "hydrogenated vegetable oils" or "refined cottonseed oil" on a label to the ultimate housewife, to us who make them they are the result of painstaking care in each process from refining to packaging. Each step must be "right," first to make a quality product but, equally important, to insure efficiency in the operation. While this efficiency does, of course, affect the profits of each company, the elimination of "waste," whether it be of raw materials, processing materials, equipment, or labor, eventually reflects on the cost of our products to the consumer and thus has its part in making the standard of living of our country. For our purpose the start of this trail is in the refining of crude oils.

Refining of Crude Oils

In addition to neutral fatty glycerides, the crude oils of commerce contain free fatty acids, phosphatides and gums, coloring matter, insoluble matter and settlings, and such miscellaneous unsaponifiable materials as sterols. The purpose of the refining step is to lower the level of these nonfatty glyceride materials to zero or at least to negligible values. The quantities of these materials present in the crudes vary with the type of oil (cottonseed, soybean, coconut, lard), with the manner in which the oil is obtained from the original raw material (expelling, extraction, wet or dry rendering), with any pretreatment that the oil may be given, such as degumming, as well as with the season and geographical source. For these reasons the refining process cannot be set on a fixed procedure for optimum results but must be varied to suit the characteristics of the crude stock.

In the very early days fats were washed with mineral acids in order to coagulate the impurities; this is still the case for some fats intended for inedible use. While one process now being practiced uses an organic acid for degumming, practically all edible fats the world over are refined with some type of alkali. The addition of an alkali solution to a crude oil brings about a number of chemical and physical reactions. The alkali combines with the free fatty acid present to form soaps; the phosphatides and gums absorb alkali and are coagulated through hydration or degradation; much of the coloring is degraded, absorbed by the gums, or made water-soluble by the alkali; and the insoluble matter is probably entrained with the other coagulable material. With heat and time the excess caustic can also bring about the saponification of some of the neutral oil. While all of these reactions have not been completely explained because of their complexity, it is of interest to note some of the physical changes that occur. The sketches shown in Figure 1 are representative of the appearance, under a microscope, of various stages of the refining of cottonseed oil with caustic soda solution. When the lye is first added (A), the mixture appears to be an emulsion with the individual drops clearly seen and evenly dispersed. Each drop seems to be surrounded by a darker layer and this outer "skin" in turn by very small individual droplets that are near the skin surface but do not touch it. A cloudy, amorphous material appears to be spread throughout the continuous phase. With continued time in the cold (B), the drops begin to gather in groups in a net of the amorphous material, with clear oil showing between the groups. At this stage the droplets, which formerly appeared to surround the main drops, now adhere directly to them and give a ''pincushion'' effect. As heating begins (C), cloudy masses form, and the drops begin to lose their identity. Much more clear oil is seen between these masses. At the end of the heating period, when the temperature has reached 140-150° F. (D), the cloudy masses contract and become translucent and shiny, probably by melting or coalescence. Very few individual drops can be seen. This is the final ''break'' familiar to all who have batch-refined oil, and the batch is ready to settle.

The process described above is typical of the open-kettle, batch-refining process, which was used for many years prior to the advent of continuous centrifugal refining and is still used in an improved form and on some special oils. The kettles usually have a height equivalent to about one and one-half times their diameter, with a cone bottom, and are fittted with a variable slow-speed agitator, vertical banks of steam coils, and swing suction-pipes to facilitate the drawing off of the refined oil from the settled foots. After the crude oil is pumped to the kettle (preferably at about 75-85° F.), it is usually allowed to settle in order to remove entrained air that would later interfere with the refining. The amount and strength of caustic to be used is determined from the free fatty acid content of the crude, the standard cup loss on the oil, and from experience with the particular oil stock. With soybean oil the caustic strength is usually 12–16° Bé. with an excess over theoretical of about .25% dry sodium hydroxide. Normally cottonseed oil is refined with a slightly stronger caustic. In either case the excess used is dependent to some extent on the expected loss; higher excesses are employed for high loss or high fatty acid oils, and the total approaches the theoretical as the loss approaches the free fatty acid content. With the oil under relatively rapid agitation, the caustic is sprayed over the surface in order to insure uniform dispersion. The lye should be so chosen that a ''break'' will not appear immediately in the cold as time in this emulsified state tends to improve the color of the final refined oil. At the first sign of a ''break'' the agitation is slowed down and heat is applied. The temperature is allowed to rise to about 130–140° F., and agitation is continued at slow speed until the foots begin to settle. Should the foots be completely coalesced at this point and show signs of settling, it is best to stop the agitation. Further stirring may tear the foots and result in a poor settle and cloudy oil. After settling over-night or at least for 8 hrs., the clear oil is withdrawn by means of the swing suction and the soapstock is drained off. The refined oil may then be water-washed or filtered through a spent press to remove traces of soap.

As in other methods of caustic refining, there is usually a relationship between the excess of lye used and the refining loss and refined color. Figure 2 shows a typical example of this relationship. If the excess is not great enough, abnormally high colors will be obtained, decreasing rapidly at first as the excess is increased but apparently reaching a relatively constant minimum value at high excesses. The loss curve is directly in reverse, rising but slowly at the lower excesses and then increasing rapidly. It is the duty of the refiner to determine the excess required to balance minimum loss with minimum color.

The general kettle-refining method (as well as the continuous) may be modified by the addition of various reagents. Sodium silicate solutions have been widely used to improve separations by ''weighting'' the foots. Actually this appears to be a surface-active effect as flocculent foots can be made ''wetter'' by the use of silicate with the resultant formation of denser particles that settle out the oil phase more quickly and with less occlusion of entrained neutral oil. The silicate in the soapstock however tends to be troublesome in later acidulation for recovery of fatty material and tends to increase the amount of bowl cleaning required in centrifugal refining. The use of various polyphosphates as additives, especially for degummed soybean oil, has led to the development of a successful low-loss, kettle-refining procedure (1). In this process the foots have an entirely different character, separating more as a dark, almost liquid, phase rather than the usual ''break.''

The kettle-refining process requires long periods of settling and long contact time between oil and caustic and depends on gravity for the separation of foots and oil. With the advent of suitable centrifugal equipment for the separation of phases of different density, it was logical that a continuous refining process be developed. As early as 1893 such a process was used in Europe, and we have seen data from experiments made in this country as early as 1921. It was not until more than 10 years later (2) however that the first successful continuous-refining process was described in this country. Since that time many modifications have been evolved, including the use of soda ash, ammonia, various chemical additives, and refining in miscella.

In the conventional caustic process, proportioned amounts of crude oil and caustic solution are sent through a mixer to a heater (130–185° F.) and thence to a centrifugal separator from which the refined oil and soapstock are discharged. The refined oil is further mixed with water (5–10%), heated, and again centrifuged in order to remove residual traces of soap. The washing step can be repeated to effect a still greater removal of residual soap, followed by passage through a vacuum dryer for the removal of moisture. As in kettle refining, strength and amounts of caustic must be varied with the type of crude stock. For cottonseed oil the strength may be from 12° to as high as 22° Baumé with excesses somewhat higher than those used in kettle refining. Degummed soybean oil can be satisfactorily refined with fairly weak lyes while about 14° Baumé lye is required for nondegummed oil. An experienced operator can judge the amount of lye necessary by the character of the foots being discharged. While the straight caustic process is simple, it requires experienced judgment in the selection of lyes to yield optimum results.

The next step in the development of the continuous refining process was the carbonate or soda ash process (3), which took advantage of the nonsaponifying character of sodium carbonate. In this process the crude oil is first heated through an exchanger to about 140° F., then proportioned and mixed with a 20° Baumé soda ash solution. This is usually about 1.5 times the stoichiometric amount needed for neutralization, but, with higher-loss oils, more may be required. As the soda ash solution will not affect neutral oil, there is no danger of saponification from larger excesses. The soda ash does however neutralize the free fatty acids present, forming soap and carbon dioxide, and precipitates the phosphatides and gums. The remaining excess of soda ash reacts with much of the carbon dioxide released, forming sodium bicarbonate, thus diminishing the amount of gaseous material present in the stream. To remove excess carbon dioxide and condition the oil-soapstock for centrifugal separation, it is then heated to 195–220° F. and sprayed into a vacuum dehydrating-chamber Here the free carbon dioxide flashes off together with most of the moisture, and the temperature drops to about 160–170° F. If insufficient soda ash solution has been used, there will be an excess of free carbon dioxide to be removed at this point and oil can be lost by entrainment in the vapor stream. To bring the soapstock to proper fluidity, the stream from the dehydrator is proportioned with about 2–5% of soda ash solution, mixed, and reheated to 195–205° F. before being centrifuged. At this point the oil is essentially "refined" but is usually dark in color and difficult to bleach. To wash out this color, a caustic re-refining is required. The separated oil from the centrifuge is cooled to 85–120° F. by flowing through an exchanger, countercurrent to the incoming crude oil, and through a water cooler and is proportioned with 1–3% of 20–30° Bé. caustic soda solution. This mixture is heated to about 160° F. and again separated centrifugally. Because of the high caustic strength needed for color removal, the mixture in the centrifuge tends to separate into a three-phase system consisting of heavy dark lye, a somewhat lighter soap phase, and the light oil phase. To bring about a clean separation, a small amount of water-flush is added directly to the centrifuge bowl in such a manner as to dilute the lye and soapstock, creating a single aqueous phase that separates easily. The refined oil is then water-washed in the same manner as in the conventional caustic process.

Fairly recently (4), modifications of the soda ash process have been developed that eliminate the dehydration and rehydration steps. In one system the soda ash solution and oil are mixed and centrifuged under pressure, making carbon dioxide removal unnecessary and discharging a concentrated soapstock low in neutral oil. In another system a high excess of soda ash is used, sufficient to combine with all of the carbon dioxide released. This oil is passed through a small float-vent tank to deaerate prior to centrifuging, and no rehydration is necessary. On normal oils 2.5 to 3 times the soda ash needed for neutralization is employed, and for very low free fatty acid oils (such as degummed soybean oil), a minimum of 1% is required. This same pressure-refining system has very recently (5) been applied to the caustic refining of coconut oils, giving losses equivalent to the free fatty acid content calculated as oleic acid.

While satisfactory results can be obtained by the modified soda ash process on cottonseed oils with 2% or less free fatty acid, the excessive amounts of carbon dioxide released with higher free acid oils and the large amounts of reagent needed led to the development of the caustic soda ash or CSA process (6). By first treating the oil with just enough strong (30° Bé.) caustic solution to neutralize the free fatty acids, the formation of large amounts of gas is avoided. The further addition of about one and one-half times the stoichiometric quantity of 20° Bé. soda ash serves to complete the neutralization and precipitate the soapstock. As all of the caustic is immediately used up in the neutralization process, any possibility of saponification of neutral oil is reduced to a minimum. The soapstock produced is essentially of the soda ash type and can be put back on cottonseed meal for cattle feed.

A large number of variations of the basic refining processes have been or are being used in the United States and abroad. Among these are the ammonia process which uses ammonium hydroxide as a non-saponifying alkali (7), the "Low-Loss" method in which a regular two-stage refining process is preceded by the use of citric acid as a gum conditioner, the "Quick-Mix" method in which the oil is first degummed and then very quickly mixed with and separated from a caustic solution (8), the use of acetic anhydride as a degumming agent without the use of an alkaline reagent (9), and even the use of ion-exchange resins. One process however that appears to be definitely of value is refining in miscella (10). Miscella from a solvent-extraction plant is brought to about 40–50% concentration either by mixing prepress oil with extraction miscella or by the partial removal of solvent prior to refining. The concentrated miscella is then mixed with fairly weak caustic, about 12° Bé., using a 0.4% excess. Miscella concentration can be controlled either by the use of alternate circulated holding-tanks or by specific gravity. Care must be taken to mix miscella and caustic thoroughly in order to get complete precipitation of gums and phosphatides and full color-removal. After centrifugal separation the miscella is water-washed and stripped free of solvent. Losses are very low, and colors are excellent. The process however has the inherent dangers present when working with large quantities of solvent, is only economical in an extraction plant where the oil-solvent mixture is already available and makes it necessary for the crusher to have an outlet for refined oil.

With the many refining methods that are available, it appears difficult to decide what method of operation a refiner should use. There are however a number of factors that will, in part at least, determine the direction to be taken. If, for instance, an extraction mill has a ready outlet for refined oil as mentioned previously, it now appears that a miscella refining process would best fill the requirements. If dark cottonseed oil is a problem, there is much to recommend a two-stage refining operation, using very strong lye (25–30° Bé.) in the re-refining step. For plants handling much oil with a high free fatty acid content (more than 2%) the caustic soda ash process would probably be recommended. The standard caustic process does a good job on soybean oil and probably represents a minimum of equipment. If a plant needs some extra capacity and unused kettles are available, the additive kettle method can be considered. A soybean mill that can use gums and phosphatides in feeds should examine the merits of the ammonia process. In every case a thorough study of the present and projected needs, type or types of crude stock, characteristics of the stock, and the local situation, together with a knowledge of the available processes, will pay for itself many times over when a process is to be selected.

Bleaching of Refined Oils

Even though an oil has been well refined and water-washed, traces of a number of undesired impurities can still remain either in solution in the oil or as colloidal suspensions. Thus chlorophyll or pheophytin and their degradation products can give the oil a greenish color, the carotenoids provide yellows and reds that may be undesirable, and traces of soaps and gums are present that will later give trouble in hydrogenation or deodorization. The purpose of the bleaching operation is not only to provide a lighter-colored oil but also to purify it in preparation for further processing.

Bleaching Agents and the Bleaching Process

Although from time to time chemical bleaching agents have been used or proposed for use on edible oils, practically all such oils are now decolorized and purified by means of adsorptive clays or carbons. The clays used are neutral or acidic natural clays that have been crushed, dried, and screened or the so-called "activated" clays that have been treated with weak acid at boiling temperature, washed, dried, and screened. Active carbon is formed from a wide variety of carbonaceous raw materials (usually waste materials) by carbonization at high temperature, combined with the use of activating materials, such as phosphoric acid, metal salts, etc.

The natural clays, while not having the decolorizing power of the activated products, perform very well with respect to cleaning up residual soap and gums and normally exhibit a lower oil-retention. A natural clay will retain oil up to about 30% of its dry weight whereas the activated clays will retain about 50%, and activated carbons, even when mixed with clays, appear to retain about 100–150% of their weight as oil. Rich (11) found that the oil retentions of both activated and neutral clays were inversely related to their apparent bulk densities. In the data he reported, individual plants showed this definite relationship, but it is notable that various plants differed as much as 10% in oil retention for the same bulk density. This variation can only be attributed to differences in plant operation, differences that reflect in operating costs.

While the bleaching phenomenon is usually referred to as "adsorption" and the large surface areas of the bleaching agents do play a part, the theoretical background is not completely known. Experimental evidence (12) can be exhibited which indicates that both physical and chemical forces and reactions are involved. It has been found however that normal oil bleaching usually follows the equation for the adsorption isotherm (13), which relates the amount of material adsorbed per unit of adsorbent to the residual amount remaining:

$$X/M = KC^n$$

In this equation X corresponds to the amount of material (color) removed, M to the amount of bleaching agent (carbon, clay) used, C to the amount of color remaining while K and n are constants that are dependent on the particular system involved. By writing this equation in the log form, it is seen that a plot of log X/M against log C should result in a straight line. This is evident in Figure 3, which shows both a normal plot and the isotherms. Figure 3 also illustrates the great variability among the different types of bleaching agents. The carbon adsorbs relatively large amounts at low levels of usage but is unable to remove the final traces even at relatively high levels. This variability is related not only to the adsorbent but also to the nature of the material to be adsorbed and the conditions under which the adsorbent is used. For this reason, experimental bleaching under use conditions is the best guide when using new adsorbents or bleaching unusual oils.

The normal variables for any given bleaching system are the type of earth, dosage, temperature, and contact time. Each must be considered in the light of the system used and the oil to be bleached. As previously mentioned, the natural clays do a very satisfactory job at fairly low temperatures when the oil is readily bleachable, tend to give more stable oils, are lowest in cost, and have low oil-retention. If the oil is difficult to bleach, such as a "green" soybean oil, the activated clays will do the job without requiring the use of excessive dosages. The activated clays are however higher in cost, retain more oil, and tend to deteriorate press cloths faster. Many activated clays will also cause a rise in the free fatty acid content of the bleached oil. Carbon is normally used on glyceride oils in combination with clays; the dosage usually is 5–10% of the amount of clay used. It is effective in removing the fluorescence sometimes found in oils, in adsorbing certain impurities that are not affected by clays, and is especially effective in the bleaching of coconut oil but is the highest in cost and has the highest oil-retention.

Bleaching with most adsorbents is relatively rapid, and the usual error is to extend bleaching time beyond the optimum. Temperature is however a factor, with shorter optimum times obtained at higher temperatures. Neutral clays will bleach cottonseed oil in 10–30 min. at 195–210° F. whereas activated clays will usually give an optimum bleach at 230–250° F. It is important to mix earth and oil at a relatively low temperature, bringing the complete mixture up to the final bleach temperature. It is believed that the best bleach is obtained when the moisture in the earth is removed in the presence of the oil. As atmospheric oxidation can darken a bleached oil, temperatures above 220–230° F. should be employed only when operating under vacuum or an inert atmosphere. Excessive contact time at any temperature usually tends to darken the oil.

Bleaching Equipment

Contact bleaching is normally carried out either batch-wise in open kettles or under vacuum, or continuously under vacuum. Batch bleaching in open kettles is the oldest and simplest method and is still in use in many plants. The oil is charged to a kettle fitted with a paddle agitator and steam coils, the agitation and heating are started, and the earth is added at about 160–180° F. Agitation is continued for a time after temperature has been reached and, when bleaching is completed, the oil is filtered through plate and frame presses to storage. When a press is full, it is blown with air or steam to remove as much oil as possible and the press is opened for cleaning. Because of its high surface area, spent clay from the bleaching of unsaturated oils tends to undergo spontaneous combustion, and care must be taken both in blowing presses and in handling the resultant cake.

The use of activated clays and higher temperatures in bleaching led to the need for protection from atmospheric oxidation, and the vacuum bleaching system was developed. The process is similar to the open kettle bleach except that it is conducted in a closed vessel under a vacuum of 27–28 in. The adsorbent can be added either as an oil slurry from a separate clay slurry tank or be sucked in directly through a valved line leading from a hopper above the vessel to below the surface of the oil. When bleaching is completed, the oil is cooled sufficiently to avoid oxidative effects, the vacuum is broken, and filtration is carried out in the normal manner.

Continuous vacuum bleaching-systems were proposed many years ago, but probably the first commercial operation was started about 1940 (14). This process was described by King and Wharton (15) and later in a modified form by Singleton and McMichael (16). The oil to be bleached is first deaerated and dried by spraying into the lower chamber of the vacuum bleaching-vessel at about 130° F. Deaeration is aided by a small steam sparge below the oil level. The deaerated oil is then heated to about 210–240° F. by passing through an economizer countercurrent to the hot oil leaving the system and by using a steam exchanger. This hot oil is first filtered through a closed press containing the spent clay from a previous batch and thence to the upper bleaching section of the vacuum vessel. A clay slurry is made up continuously from bleached oil and metered clay in a separate agitated slurry tank. This final slurry is fed, again through a spraying device, into the upper portion of the bleaching vessel where it is mixed with the main stream of oil. Here, too, sparge steam aids the mixing, and steam coils maintain the temperature. After about 10 min. of average residence time, the oil is filtered through a clean press, partially cooled by means of the previously mentioned economizer, and finally water-cooled to 130–150° F. before being sent to storage.

As in all other processing steps, when setting up a bleaching procedure, one must keep in mind both the final objectives to be reached and the effects on or of any intervening processes. The kind and amount of earth or carbon used need only be sufficient to clean up the oil preparatory to hardening or deodorization and to remove any undesirable color that will not be removed in these later steps. The minimum required bleach is usually the best as overbleaching can lead to flavor, oxidative, and even color instability. Open-kettle bleaching can be very effective as long as care is taken in the selection of earths and the control of temperature. Vacuum bleaching has the advantage of removing the influence of atmospheric oxidation when the more active earths or higher temperatures are employed. The advantage of continuous bleaching is manpower saving rather than the effectiveness of earth usage. One troublesome point however has been the regulation of clay dosage. With bulk shipments of clay there are savings both in earth and in handling costs. All of these factors must be considered in the selection of a process for an individual installation.

Deodorization

Most of the major oils in use in this country today retain, even after refining, certain undesirable odors and flavors. Normal bleaching imparts an "earthy" odor while hydrogenation adds an odor that can only be described as "typical" and certainly undesirable. To provide the bland and almost odorless fats and oils required by today's consumers it is necessary that these undesirable impurities be removed by deodorization.

In essence, deodorization is a steam distillation, carried out under vacuum, in which small quantities of the more volatile components are stripped from the oil, leaving behind only the bland, nonvolatile, essentially triglyceride constituents. In addition to the removal of odoriferous materials however the deodorization process also serves to reduce the free fatty acid content of the oil to a desirable low level, to destroy the peroxides present, and to improve the color by breaking down carotenoid pigments. By assuming that the volatile constituents in the original oil would follow Raoult's law and Dalton's law of partial pressures, Bailey (17) derived an equation relating many of the variables involved in deodorization. From this equation it can be seen that the amount of steam required (or the time required at a definite steaming rate) is directly proportional to the batch size, the absolute pressure in the deodorizer, and the logarithm of the ratio of initial to final concentrations of the volatile substances, and inversely proportional to the vapor pressures of the volatile substances at the operating temperature and the vaporization efficiency of the process. While the effects of these variables have been noted in practice, the equation serves to emphasize their relative magnitudes and interrelationships.

Although the usefulness of blowing oils with steam to improve odor was recognized in the early 1890's (18), it was apparently not until about 1900 that David Wesson started treating oil under vacuum in this country. This system has been used for many years, and large quantities of oil are being processed in this manner today. In the batch system the oil is charged directly into the deodorizer or "still," which is held under vacuum at all times. A small amount of sparge steam is turned on to provide agitation as soon as loading starts, and the charge is heated either by coils within the vessel itself or by circulating the oil through an external heat exchanger. Heat is usually provided either by high pressure steam or Dowtherm. Vacuum may be maintained by wet vacuum pumps, but these have been almost entirely supplanted by steam jet ejectors with three or more stages. After the oil has been held at deodorization temperature for the required time, the oil is cooled either in the deodorizer itself or more often in separate "drop" tanks or cooling stills or by means of external tubular coolers. The cooled oil is usually sent through a "polishing" press to remove any haze or polymerized particles before being pumped to storage.

Batch deodorizers are usually of about 20–30,000 lbs. capacity although units from 5,000 to 60,000 lbs. capacity have been used. Deodorizations are carried out at the highest available vacuum; a three-stage system provides 6–8 mm. of absolute pressure. The temperature of deodorization is dependent to some extent on the oil being processed, being somewhat lower for liquid oils than for hydrogenated products. In the United States about 375–450° F. is common practice with some deodorizations being carried out at even higher temperatures. In Europe the trend is to use lower temperatures, in the 340–375° F. range. Because of variations in operating pressure, both deodorizing times and total stripping steam used may vary widely. Normally however deodorization will be completed in 2–5 hrs. with the use of 5–15% of total stripping steam, based on the charge weight.

As in all of our other processing steps, there were many early attempts to realize the advantages of a continuous system in deodorization. One of the earliest of these (19), taking advantage of petroleum refining experience, makes use of a bubble cap column to bring about intimate contact between oil and stripping steam. The oil, deaerated in a separate chamber, is heated and fed to the top bubble-cap tray, gradually moving downward countercurrently to a rising flow of steam. Although a vacuum of 6 mm. is provided at the top of the tower, pressure drops across the trays increase this pressure to about 20 mm. at the bottom. As the retention time in the tower is only about 20 min., it is necessary to use higher operating temperatures (445–480° F.) to achieve the desired results. Another truly continuous deodorizer (20) consists of a series of individual vessels under very high vacuum through which the oil flows in sequence. Temperature, vacuum, and sparge steam are controlled in each vessel. The oil is gradually heated while passing through the earlier stages and is cooled in the later stages. This system has proven extremely satisfactory with respect to both quality and efficiency, but the process and equipment have not been put on the market commercially.

One deodorizer that has achieved considerable commercial success both in this country and abroad is the semicontinuous unit manufactured by the Girdler Corporation (21). An outline diagram of this unit is shown in Figure 4. The unit as shown consists of five trays stacked inside of, but not quite contacting, an outer shell. Each tray is fitted with a steam sparge and is capable of holding one-half of the hourly capacity of the unit when filled to a depth of about 24 in. By means of a measuring tank, oil is charged to the top tray where it is deaerated while being heated with steam to about 320–330° F. At the end of a half-hour period the charge is automatically dropped to the second tray, and the top tray is refilled. In the second tray the oil is heated by Dowtherm to operating temperature and, again after a half-hour period, is automatically dropped to the tray below. When the oil reaches the bottom tray, it is cooled to about 130–150° F. and discharged to a drop tank from which it is pumped to storage. As each tray is independent within the shell, the shallow pool of oil in each receives the benefit of the full vacuum. As the trays support only the weight of the oil, rather than the outer atmospheric pressure, they can be made of light-weight resistant metals, such as pure nickel, without unduly increasing the cost. Each tray is fitted with splash baffles that greatly increase the stripping efficiency of the steam and with secondary baffles that eliminate entrainment. Any vapors leaving the tray, which tend to condense, will do so on the outer shell and run down this outer shell rather than reflux back into the oil. The efficiency of the unit has led to its fairly widespread acceptance.

Deodorization is the last major processing step through which the flavor and odor and many of the stability qualities of an oil can be controlled. From this point onward effort is directed only toward retaining that quality which the oil then possesses. For this reason, considerable care must be given to the selection, operation, and maintenance of deodorization equipment. Because of the high temperatures involved, it is particularly advisable to avoid the use of metals having prooxidant characteristics. Carbon steel has long been used at temperatures below 390–400° F., but nickel or stainless steel is preferred, especially at higher temperatures. Welded construction will give fewer chances for air leaks, and the vessels should be well insulated to minimize heat loss. Long vapor lines are to be avoided as they reduce the efficiency of the vacuum system and, if improperly placed, will tend to promote the undesired reflux of condensed vapors. There is some question as to the usefulness of baffles for the prevention of entrainment in batch deodorizers having ample headspace, but in the limited headspaces common to the continuous or semicontinuous deodorizers they are a necessity. Inefficient or excessive sparging can lead to considerable entrainment loss, and sparge steam containing air or impurities from boiler water treatment can lead to puzzling flavor results in otherwise good oil. Again, to avoid oxidative effects, the oil should be well deaerated before reaching deodorization temperatures and should be cooled to below 140–160° F. before being discharged to the atmosphere. Local overheating, whether it be from coils exposed above the oil level or from the use of too high a temperature gradient at the heating surface, must be eliminated in order to avoid off-flavors. While many of these points are obvious, they are all important to the attainment of top quality in fats and oils.

Stabilization

With the attainment of a quality oil, efforts must be made to preserve that quality. Since the dawn of history and the passing of the days of kill-and-eat, man has sought ways to protect and preserve his foodstuffs. Fats and oils, while relatively immune to microbiological spoilage, are particularly subject to spoilage resulting from oxidative action, and it is this type of spoilage that has gained (and merited) the most attention.

The mechansims of the autoxidative reactions that bring about rancidity are complex and much has been written on the subject (22), but much still remains to be explored. For the present it must suffice to say that the unsaturated bonds present in fats and oils create susceptibility to attack, that the reaction is autocatalytic, that unsaturated hydroperoxides are apparently the primary reaction products, and that further changes in these primary products lead to the formation of odoriferous aldehydes, ketones, and acids. Because of the oxidative weakness of double bonds, the greater the unsaturation in an oil, the greater are the possibilities for rancidity development. The active methylene groups between the double bonds in polyunsaturated compounds are particularly susceptible to oxidation; thus oils containing such acids as linoleic or linolenic are likely to oxidize more rapidly. These tendencies are, of course, greatly modified if natural or added antioxidants are present. At least the initial reaction involved in fat oxidation is believed to be a chain effect; the peroxides formed act as oxygen carriers.

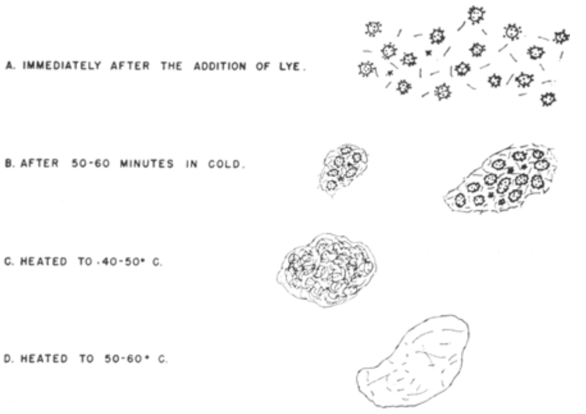

FIG. 1. Caustic refining process under the microscope.

The mixing of rancid fat with fresh fat thereby serves to promote the rancidification of the entire mixture. Practically all of the methods for estimating the extent to which a fat has been oxidized are dependent on the measurement of one or another of the products of the reaction. The determination of peroxide content (22, 23) is probably one of the most widely used. The estimation is based on the fact that iodine is liberated from acidified potassium iodide solution by peroxidic oxygen. Care must be exercised in applying this test as a number of conditions, such as high temperature, will cause some peroxides to break down while others are still being formed. Many other qualitative and semi-quantitative tests, such as the Kreis test, are based on reactions of the aldehydic or ketonic by-products. In recent years considerable research has been aimed at the direct determination of carbonyl compounds (24). Many workers feel that such a determination can be made more specific for rancidity or prior oxidation than can the peroxide test.

While long-term storage tests, under use conditions, are the safest for the determination of oil stability, there is a constant need for accelerated methods that will indicate the susceptibility of a fat toward rancidity development. The most commonly used accelerated tests include modifications of a) the active oxygen method (25) which depends on measuring the peroxide content of an oil after heating and aerating under controlled conditions, b) the Schaal Oven test (26) in which samples are observed organoleptically during storage in an oven, and c) the oxygen absorption method (27) in which the uptake of oxygen with time at higher temperatures is measured.

As with most oxidative reactions, the oxidation of fats requires the presence of a susceptible material, a source of oxygen, and the application of energy to promote the reaction. It is through the elimination of one or more of these factors that we try to prevent or retard oxidative rancidity. By the careful selection of raw stocks we can reduce the probability of oxidation and, where possible, we can decrease or eliminate the more susceptible components through hydrogenation or fractionation. Mishandling of stocks, even in the crude state, can destroy natural antioxidants, and the optimum quality of the oil can never be realized. While it is practically impossible to shield oils from oxygen at every step from crude to consumer, many unnecessary sources of aeration can be avoided. Pumps with air leaks on the suction side, tank-filling lines that cause splash and air entrainment, agitators that swirl and draw in air, and leaks in vacuum vessels, all can be corrected. Storage tanks, tank cars, and some consumer packages can be blanketed with inert gas. Again, it is impossible to process and transport fats and oils without subjecting them to heat, but the heat and the effects of the heat can be minimized. Temperatures can be held as low as practicable and local overheating avoided; where high temperatures are needed, special precautions can be taken to avoid air contact. As oxidized fat and heavy metals, such as iron and copper, catalyze the oxidative process, sources of such contaminants should be eliminated. Oxidized oil must not be allowed to accumulate on the sides of tanks or presses, in pipe lines, or in filling equipment. Copper and brass fittings and many copper-containing alloys should be removed from any fat-handling system, and iron should be avoided wherever higher temperatures are encountered.

Although the processor makes every effort to protect his fat products, it is practically impossible to avoid some traces of the heavy metals, and impossible for him to control the handling of the product once it has passed to the consumer. For these reasons, further precautions must often be taken to preserve the quality of the product. The trace metals present or with which the fat may come in contact, can be inactivated through the use of chelating or sequestering agents. These agents, such as citric acid, phosphoric acid, tartaric acid, and many others that have been proposed (28), complex the metals so that they no longer have a catalytic effect. They can be used effectively both during processing (immediately after deodorization) or in the form of a final addition, and only extremely small amounts are required. Many of the natural fats contain inhibitors (such as the tocopherols or sesamol), which apparently react in such a manner as to stop the chain reaction of the oxidative process. These inhibitors or "antioxidants" are present in fats in varying degrees. The animal

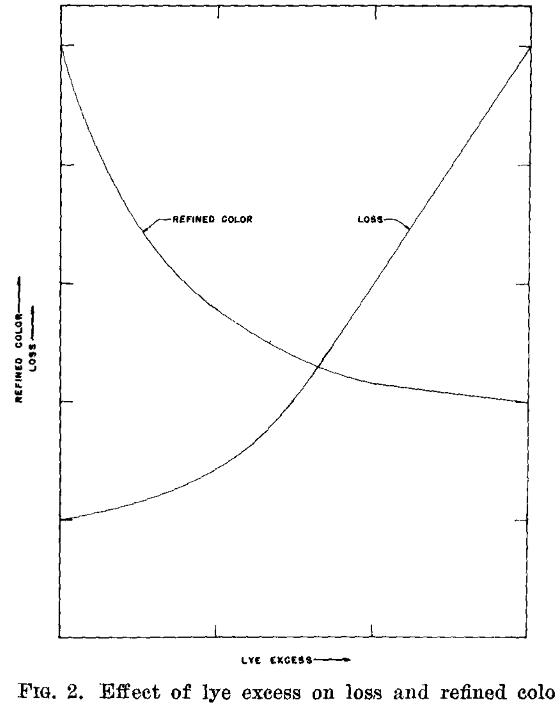

FIG. 2. Effect of lye excess on loss and refined color.

fats are practically devoid of natural inhibitors. For this reason the processor must often add antioxidants in order to extend the shelf-life of his fats and the products made from these fats.

The literature is filled with references to materials that have been proposed as antioxidants, but relatively few, such as butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), nordihydroguaiaretic acid (NDGA), and propyl gallate, etc., have been used commercially. Their use is regulated in this country by the Food and Drug Administration and by the Meat Inspection Division of the U.S.D.A. (29). All additions of sequestrants or antioxidants must conform to the regulations set forth by these bodies. The choice of antioxidants is dependent not only on the fat concerned but also on the use to which it is put (30). Many of the antioxidants (such as propyl gallate) tend to develop off-colors when in contact with metals and moisture. Others are particularly susceptible to heat and provide little "carry-through" into baked products. In many instances a combination of antioxidants will act synergistically and provide more protection than a single product or will provide necessary shelf-life as well as carry-through. Thus the "best" antioxidant is the antioxidant or combination that works best for the particular application.

Plasticization of Shortening and Margarine

As we all know, when shortening or lard in the liquid state is allowed to cool slowly, the more saturated glycerides will crystallize first, the crystals growing in size until, at room temperature, a grainy, pasty mass is obtained. This grainy material is not only unsightly and difficult to handle but lacks many of the basic qualities that are desired in a shortening or margarine. For shortening it lacks the creamy smoothness, the air content, and the crystal structure that are required for ease in batter mixing and the development of proper volume and texture in cake baking. There would be a lack of homogeneity in both shortening and margarine, and the printing of margarine would be impossible. To achieve these desirable qualities the fat must be chilled quickly or "plasticized."

Probably the earliest device in general use for achieving the rapid cooling of fat was the so-called chill or lard roll. The roll was a hollow, horizontal cylinder fitted for internal cooling by means of brine or ammonia. By rotating the lower portion of the roll through a pool of molten fat, a relatively thin film was picked up and cooled below its crystallization point as the drum rotated; the semi-solid layer was scraped off by a doctor blade. The supercooled fat then dropped into a horizontal trough or picker pan, in which a longitudinal shaft carrying a number of paddle blades rotated. As the fat was supercooled, crystallization would continue in the picker pan while the paddle blades beat in air, creamed the product, and moved it toward the discharge end. At this point a steam pump picked up the shortening and forced it at high pressure through a small orifice or slot in order to complete the homogenization of air and oil and minimize graininess. While the process was a vast improvement over chilling in water and while some people still insist that today's margarine isn't as good as the roll product, the chill roll had many faults with respect to control and efficiency.

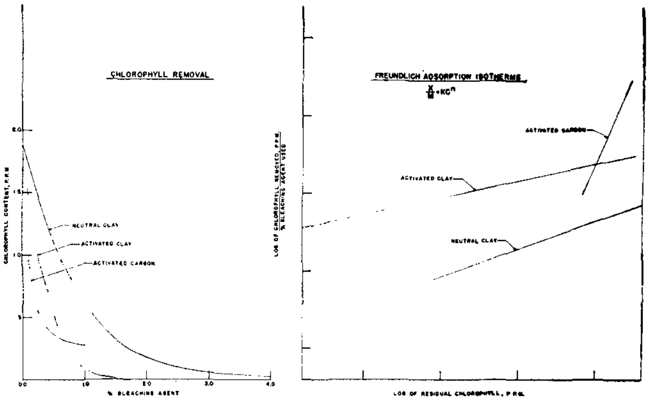

FIG. 3. Effect of bleaching agents on chlorophyll removal from refined soybean oil.

In the early 1930's work aimed at the development of improved heat-transfer equipment for the freezing of ice cream led to the perfection of a continuous internal chilling machine that was soon applied to the plasticization of shortening and margarine (31). The liquid fat or margarine emulsion to be chilled is pumped into the relatively small annular space between the outer jacket, through which the refrigerant passes, and the large inner mutator shaft. As the oil contacts the cold jacket wall, it congeals but is instantly scroped off by two rows of floating scraper blades attached to the rapidly rotating mutator. This repeated high-speed congealing-scraping sequence provides extremely high heat transfer rates and a homogeneous product. The mutator may be hollow and heated slightly by means of warm water in order to prevent the formation of adhering masses of crystallized fat.

In the usual shortening plasticizing process (32) the fat, at about 130–160° F., is fed to a constant-level tank and then picked up by a gear pump, which maintains a pressure of 300 to 400 lbs. p.s.i. on the chilling system. Air or nitrogen is introduced into the suction side of this pump in sufficient quantity to provide about 10–15% by volume in the finished product. The oil and air mixture leaving the pump is brought to about 115–120° F. in a water-cooled exchanger before passing through the Votator unit, which is generally cooled by the direct expansion of ammonia. All-vegetable shortenings will normally leave the chiller at about 55–60° F., and animal fat products about 10° higher. While very fluid, this supercooled fat will set up rapidly if allowed to remain quiet for but a moment. In order to complete the crystallization while retaining a fine crystal structure, the fat from the chiller is sent through a cylindrical "B" unit (or two in series) equipped with a rotating longitudinal shaft having prongs that intermesh with stationary prongs projecting from the sides of the cylinder. This "working B" unit has the effect of the previously-mentioned picker pan. Because of the crystallization taking place, the temperature of the fat will rise about 15–25° F. while passing through the unit. The fat from the "B" unit, still under pressure, is then extruded through a texturating valve; the sudden reduction in pressure releases the occluded or dissolved air or nitrogen in the form of microscopic bubbles, and the shearing action further homogenizes the mixture. A second gear pump is then used to bring the pressure back up to 300–400 p.s.i.g. and deliver it through a second texturating valve to the filling equipment. The chilling of margarine is a similar process except that "quiescent B" units and lower operating temperatures are used in order to provide a firm body suitable for printing rather than the creamy consistency desired in shortenings.

Although no chemical changes take place in the plasticizing operation, the physical changes brought about affect both the appearance and the utility of the product. Before the fat enters the chilling system, care must be taken to have the temperature constant to insure uniformity of cooling. Drawing from a constant-level tank is necessary to provide a constant feed rate and, through this, a constant ratio of air or nitrogen to oil. Unless the air is controlled and properly distributed, streaks may result and fill levels will vary. Streaking will also occur if pressures fluctuate or texturating valves are clogged or out of adjustment. The accumulation of hard stock on the mutator can result in poor product texture and can throw the scraper blades out of proper alignment. Residence time and shaft speed in the "B" unit must be so controlled as to allow fairly complete crystallization together with sufficient working to give a smooth body. The rise in temperature or "kick" in the package because of further crystallization should be as low as possible, usually less than a few degrees. Even with the product in the package however processing and the need for careful control is not finished as tempering plays an important part in the attainment of quality. This will probably be touched upon in a later paper.

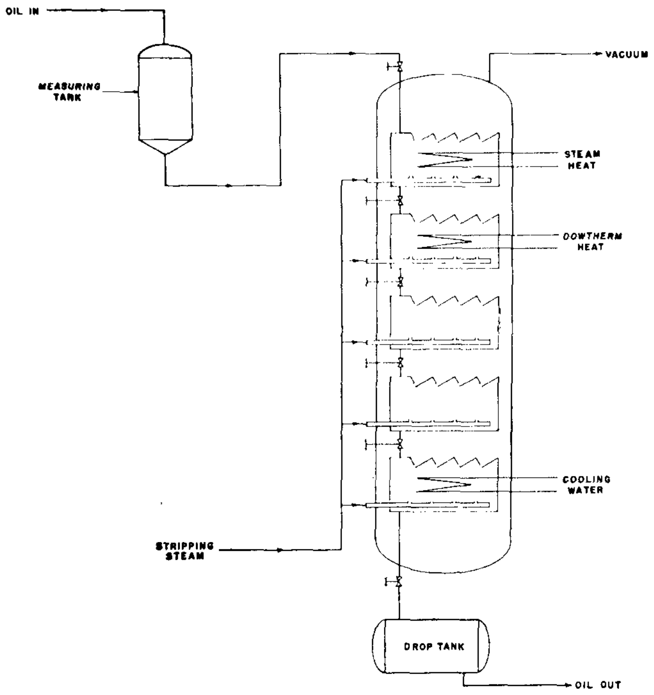

FIG. 4. Semicontinuous deodorizer.

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