Storage, Handling, and Transport of Oils and Fats

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1. INTRODUCTION

Damage to oils during storage, and the resulting loss in quality and yield, can occur because of deterioration-adverse chemical changes caused by the intrinsic nature of oils; contamination from natural substances associated with the source of the oil, traces of pesticides, and that introduced by oil processing or in transit; and adulteration-deliberate admixture of one oil with another.

1.1. Deterioration of Oils and Fats

Hydrolysis, the reaction of fats and oils with water, and *oxidation*, the chemical reaction in which oxygen combines with another substance with the liberation of heat, are the two basic processes that result in the deterioration of oils and fats. Oxidation is mostly responsible for much more of the deterioration of fats and oils than hydrolysis.

Moisture promotes the splitting of triacylglycerols to form free fatty acids, mono- and diacylglycerols (Figure 1), which result in increase of refining losses directly related to the free fatty acid content of oils and fats. Essentially, hydrolysis

Figure 1. Hydrolysis of fats and oils.

is the reverse of making a fat molecule. This process typically requires a fat-soluble catalyst, high temperature ($>100\,^{\circ}$ C), and long time (several hours) (1). Partial hydrolysis of lipids typically occurs because of improper seed storage and handling, such as high moisture content, high temperature, and seed mechanical damage. Such reaction is usually catalyzed by the lipases naturally present in the oilseeds. The conditions used during oil extraction can also significantly affect such lipase catalyzed reaction (2). The deterioration of a fat or oil in the presence of oxygen is termed oxidative rancidity. The initial step in the oxidation of an oil or fat is the addition of oxygen at or near the double bond of a fatty acid chain to form unstable compounds generally designated as peroxides (Figure 2) (3).

There are three types of lipid oxidation: autoxidation, photo-oxidation (or photo-oxygenation), and enzyme-catalyzed oxidation. Lipid autoxidation is a free radical chain reaction that involves the initiation, propagation, and termination steps. The initiators for the initiation reaction are free radicals produced by (1) thermal dissociation of hydroperoxides, (2) metal-catalyzed decomposition of hydroperoxides, and (3) photosensitization of certain chemicals (4). The initial peroxides can either be impurities or formed between lipid and the very active singlet oxygen (1500 times more active than triplet oxygen), which is essentially photo-oxidation. Singlet oxygen is produced from the ordinary triplet oxygen by light in the presence of a sensitizer, such as chlorophyll and methylene blue. Singlet oxygen is added directly to the double bond by the concerted "ene" addition mechanism, and the peroxides formed are different from those formed by autoxidation (4). Photo-oxidation is not a chain reaction and is not affected by free radical quencher type of antioxidant, but

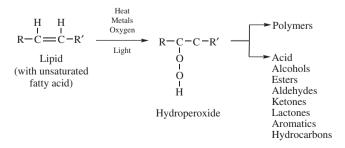


Figure 2. Oxidation of fats and oils.

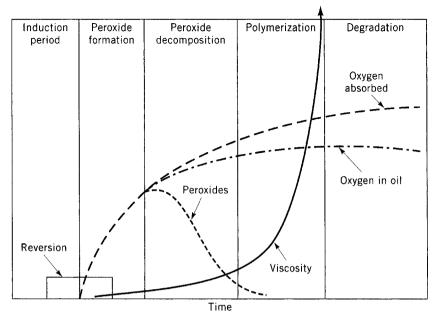


Figure 3. Stages of progressive deterioration of fats through oxidation (5).

the reaction is inhibited by singlet oxygen quenchers such as carotenoids. Direct photo-oxidation of lipids is generally of less concern than autoxidation because light absorption at less than 220 nm cannot reach lipids unless they are exposed to sunlight or fluorescent light without proper protection. The peroxides initially present in the oil as impurities can also be produced by enzymatic oxidation. Various lipases and lipoxygenases are naturally occurring in plants or animals. The enzyme-catalyzed oxidation start with the hydrolysis of the lipid, and then only the polyunsaturated free fatty acids (pentadiene) are oxidized by lipoxygenases.

When the oxidation of an oil is followed experimentally, either by measuring the amount of oxygen absorbed or determining the peroxide value, the course of oxidation is defined by the oxygen absorbed in the oil, as shown in Figure 3 (5). During the initial or induction phase, oxidation proceeds at a relatively slow and uniform rate. Peroxides are formed during this period at a faster rate than they are destroyed so that their content increases in conjunction with the oxygen absorption. After a certain critical amount of oxidation has occurred, the reaction enters a second phase, characterized by a rapidly accelerating rate of oxidation. The point at which the sample begins to smell and taste rancid coincides with the beginning or early part of the second phase. As oil oxidation continues, with time, the peroxides that are formed decompose to generate volatile and nonvolatile compounds that contribute to flavor and odor deterioration of oils and fats. The extreme stages of oxidation, polymerization, and degradation are accompanied by rapid increase in the viscosity of the oil. There is considerable variation among different fats in the manner in which their oxidation and accompanying flavor deterioration proceeds. The

TABLE 1. Relative Reaction Rate of Fatty Acids with Oxygen (6).

Fatty Acid	Approximate Relative Oxidation Rate (PV formation)
Oleic acid (C18:1)	1
Linoleic acid (C18:2)	10
Linolenic acid (C18:3)	25

amount of oxygen that must be absorbed to produce rancidity will vary according to (1) composition of the oil (2) presence or absence of antioxidants and pro-oxidants, and (3) conditions of oxidation.

Generally, oxygen absorbed will amount to about 15–150% of the oil by volume or 0.02–0.20% by weight. Fats high in oleic acid and low in linoleic acid will

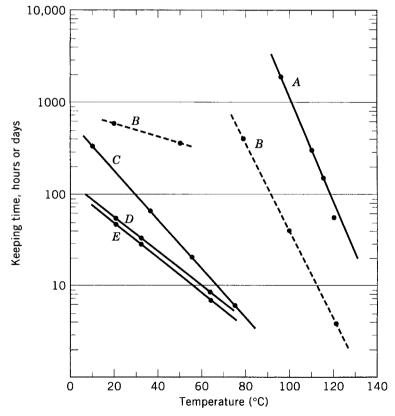


Figure 4. Effect of temperature on the rate of oxidation of various fats: (A) Miscellaneous commercial shortenings aerated until rancid, (B) pure methyl oleate aerated to peroxide value of 500 meq/kg, (C) purified methyl esters of mixed soybean oil fatty acids aerated to a peroxide value of 500 meq/kg, and (D) and (E) commercial vegetable oil shortenings incubated at 65 °C and stored at 21 °C and 32 °C until rancid.

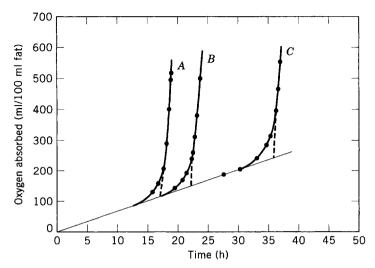


Figure 5. Oxygen uptake at 90°C of (A) corn oil, (B) corn oil plus 0.02% lauryl caffeate, and (C) corn oil plus 0.10% lauryl caffeate.

become rancid after the absorption of more oxygen than fats in which the ratio is reversed.

The relative oxidation rates of pure fatty acid esters based on peroxide formation are shown in Table 1 (6). This table is based on a common factor of one that has been arbitrarily assigned for the oxidation rate of oleic acid.

The rate at which oxygen is absorbed is markedly accelerated by heat and by exposure to light, particularly in the ultraviolet and near-ultraviolet range (7, 8). The effect of temperature on the rate of oxidative deterioration is shown graphically in Figure 4 (9). The coefficient of reaction increased markedly above $60 \,^{\circ}\text{C}$ $(140 \,^{\circ}\text{F})$.

As shown in Figure 5, oxygen uptake relates directly to the chemical reactivity of the edible oil. This effect becomes even more pronounced during the later stages of storage. The phenomenon of a reduced induction period, resulting in shortened product shelf life, is also shown in Figure 6 (10). For example, as shown by curve C, organoleptic rancidity occurs in an oil with good stability after 70 h of storage. Organoleptic rancidity occurs at a much more rapid rate in curves A and B which illustrate the effect of a reduced or shortened induction period.

Oxidation has an important effect on the color of fats and oils. Although oxidation bleaches the carotenoid pigments, it tends to develop the color of other types of coloring material and, in certain cases, even develops colored compounds of quinoid nature from the fatty acids or acylglycerols of the oils. Cottonseed and, in certain cases, soybean oil are subject to marked darkening upon oxidation. The effect of oxidation or aeration on the color stability of oils is shown in Figure 7 (7).

Effects of temperature and oxygen concentration on oxidative deterioration during storage of crude sunflower oils, obtained by pressing and solvent extraction, were studied (11). Extracted oil showed a higher oxidative stability than pressed oil.

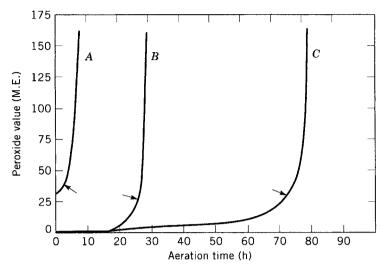


Figure 6. Stability tests (aeration at 110°C) of (A) hydrogenated peanut oil after oxidation to near rancidity, (B) oxidized oil after steam deodorization, and (C) hydrogenated peanut oil. (Arrows indicate points of organoleptic rancidity.)

This may be attributed to the presence of more polar protective antioxidants in the solvent-extracted product. As expected, oxidative deterioration was strongly dependent on temperature, oxygen availability, and the ratio of exposed surface to sample volume.

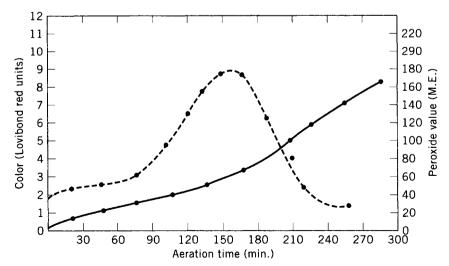


Figure 7. Effect of oxidation (aeration at 120°C) on the color of refined and bleached cottonseed oil.

1.2. Flavor and Odor Stability

Many fats and oils develop off-flavors during storage, which has been called reversion, that is, oil flavor reverting to the original flavor of the crude oil. However, as discussed by Smouse (12), this is more accurately called retrogression because the flavor retrogrades from a better to a worse condition. Also, aged oils do not develop off-flavors identical with that of the crude oils, but for any given type of oil, it is always specific and characteristic. Although all oils develop off-flavors, some do so at a faster rate than others. Soybean and marine oils develop "fishy" flavors, lard and tallow develop "animal" flavors, rapeseed and linseed oils develop "grassy/ painty" flavors, and palm oil develops "painty/rancid" flavors. All of the efforts to prevent the development of off-flavors in oils are aimed at slowing down the rate at which they develop. Multivalent metals, such as iron or copper, act as pro-oxidants when present with triacylglycerols. Research at the U.S. Department of Agriculture (USDA) National Center for Agricultural Utilization Research (NCAUR) in Peoria, Illinois showed that metal inactivators, which chelate or sequester these metals, were very effective at reducing the rate of reversion in sovbean oil (13). This was a major improvement in processing for soybean oil stability and is practiced universally by the industry. Recent research (14) has indicated that citric acid addition to canola oil is important for flavor stability in the oil. A good discussion of the theories of sovbean oil reversion is presented by Smouse (12), which includes 121 citations to pertinent research. Each theory is discussed in detail: linolenic acid theory, isolinoleic acid theory, oxidative polymer theory, phospholipid theory, nonsaponifiable theory, multivalent metals, and singlet oxygen. Each of the theories plays a role in soybean oil reversion.

1.3. Additives and Stability

Perhaps the most important additive of edible oils to enhance stability during storage and transport is citric acid or a similar metal chelating agent (15). Traces of metals in a reactive form act as catalysts that greatly promote the autoxidation of fats and oils. Concentrations of iron as low as 0.1 ppm or copper as low as 0.01 ppm can accelerate the deterioration of soybean oil (16). If an oil has higher concentrations of metals, it is necessary to first lower the content by a vigorous acid wash of the oil, for example, with very dilute phosphoric acid or by use of activated bleaching earth to absorb metals and metal complexes from the oil. A small amount of citric acid (i.e., 0.05% w/w, citric acid/oil) can be added to enhance the effectiveness of a bleaching earth. Some other acids that have been used to chelate metals are ascorbic, phosphoric, tartaric, and ethylenediamine tetraacetic acid (EDTA). It should be noted that citric acid does not improve the stability of olive oil (17).

Synthetic antioxidants effectively improve the stability of fats and oils with a low level of natural antioxidants, such as tocopherols, and with a low level of polyunsaturation. With oils that have a high content of polyunsaturated fatty acids and significant level of tocopherols, such as soybean oil, synthetic antioxidants

minimize the accumulation of peroxides but did not improve the flavor stability (18). The desired qualities of an antioxidant used to stabilize edible fats and oils are: (1) use in a product is safe (2) contributes no odor, flavor, or color to the product in which it is used (3) effective in the product at low concentrations (4) easily incorporated into the product (5) retained after cooking processes such as baking and frying (6) available at low cost for the application (19). Lauric-acid-containing oils are rather poor in their tocopherol content, as is the case with olive oils. However, palm oil, soybean, corn, and cottonseed oils contain higher levels of these natural antioxidants. Synthetic antioxidants were shown to be effective in the stabilization of virgin olive oil (17). Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary-butylhydroquinone (TBHQ) all improved the oxidative stability of the olive oil during storage at 50°C (122°F) in the dark but were not effective in preventing photo-oxidation of olive oil. It should be noted that addition of antioxidants to oils, which are already deteriorated, will not improve the quality or stability of the oil. Thus, it is of importance to produce a fresh quality material and immediately protect it with either nitrogen or antioxidants.

1.4. Antioxidants as Processing Aid

Antioxidants are of extreme help in protecting the quality of the oils during transport, storage, and processing, and finally, when the oil is deodorized, these are partially removed. TBHQ plays a major role in providing protection by addition right in the crude oil at levels of 200 ppm together with 50 ppm of citric acid. This not only saves the oil from degradation but also improves the final yield of the processed oils, thus economics of addition of antioxidant can be very well balanced by improved yield with better profitability and less worries during processing.

1.5. Contamination of Fats and Oils

Contamination begins in the fields and is possible at all stages of processing and application. The sources of contamination are several and some are found before the primary products are processed. All agricultural products are likely to contain evidence of the environment from which they come: dirt and dust, fragments of vegetable matter, insect parts, and so on. Other insoluble impurities appearing in crude oils will come as precipitates from the oils themselves. Most of the farm rubbish and the materials from the original plant and from the oil itself should have been removed before the oil is shipped, but some may carryover and some extra precipitation from the oil is possible.

Pesticide residues are the most common agricultural chemicals that contaminate oils and they are almost inevitable. Although edible oils are secondary products derived from the processing of crops, there will be some carryover of pesticide residues into the oil. In 1995, a list of persistent organic pollutants (POPs) were published (20). They were classified as (1) chlorinated pesticides, such as aldrin and DDT, and other industrial chemicals, such as hexachlorobenzene and

	(4)		
	Light PAH	Heavy PAH	
Coconut	992	47	
Palm kernel	97	5	
Rapeseed	30	4	
Sunflower seed	66	12	
Palm	21	1	
Soybean	18	2	

TABLE 2. Polycyclic Aromatic Hydrocarbons (PAHs) Content of Some Crude Vegetable Oils (ppb) (20).

polychlorinated biphenyls (PCBs), or (2) bromine compounds from flame retardants, and (3) unwanted byproducts such as dioxin and polycyclic aromatic hydrocarbons (PAHs) from incineration. The PAH content of some crude vegetable oils is shown in Table 2. The light PAH is removable by deodorizer distillation, and the heavy PAH can be removed by adsorption by using activated carbon. Although there is no regulation at present about these PAHs, the desirable maximum content for heavy and total PAH is 5 ppb and 25 ppb, respectively.

Dioxin content in certain oil and its current and future maximum levels are shown in Table 3. Pilot-scale experiments have shown that dioxin can be sufficiently removed by activated carbon treatment (20). Similarly, PCBs that are present in foods in ppb level can be reduced by activated carbon or deodorization treatment of the oil.

Some oilseeds are dried in the field with hot gases from oil burners. Copra is often dried in ovens or kilns fired by coconut shells. In each case, contamination with diesel fuel fumes or polyaromatic hydrocarbons is inevitable. The only question is to what extent. Some hydrocarbons occur naturally in plants and appear in plant products. Mineral oil contamination of vegetable oil was also associated with toxic oil syndrome (20).

So long as uncoated mild steel tanks are accepted, there is a danger of mechanical contamination by rust flakes or powder or of the formation of iron salts by interaction with fatty acids in acid oils. Accordingly, such tanks are often coated with inert materials (plastics for food contact). The dangers of metal contamination can be eliminated altogether by using stainless steel.

TABLE 3. Typical Dioxin Level (pictogram toxicity equivalent/gram) in Certain Oils and its European Union limits (20).

	Typical Content	Current Max	Max After 2006
Vegetable fats	0.01–10	0.5	0.5
Crude fish oil	_	6.0	4.0
Refined fish oil	_	2.0	1.5

2. STORAGE AND HANDLING

2.1. Types of Facilities

Bulk storage and handling facilities are needed by (1) extraction plants and refineries, (2) industrial users of fats and oils, and (3) tank farm operations. The latter represent a distinct type of facility because they are not involved in the manufacture or use of edible oil products but merely store, handle, and ship them for national and international trade.

A typical bulk storage and handling facility for finished products is depicted in Figure 8. Key features include a plant for hydrogen production, hydrogenation facilities, deodorization equipment, storage tanks for partially processed and finished products, tank car and truck-cleaning facilities, and a loading line.

2.2. Crude Fats and Oils

Crude fats and oils may contain significant amounts of non-acylglycerol materials that should be removed prior to bulk storage, handling, and transport. These include gums (phospholipids), meal fines, moisture, seed fragments, and proteinaceous material. Seed fragments and cell tissue contain lipases that, in the presence of moisture, hydrolyze triacylglycerols into free fatty acids. Also, the combination of moisture, seed fragments, and mucilaginous material provides an ideal system for microbial growth that can lead to putrefaction and development of objectionable odors. These factors, coupled with the fact that crude fats and oils are usually stored

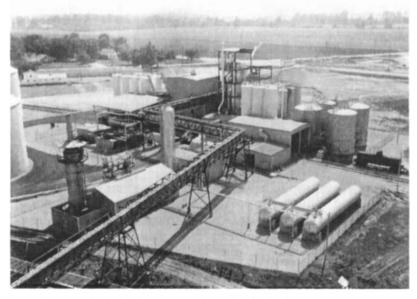


Figure 8. Typical bulk storage and handling facility for finished products.

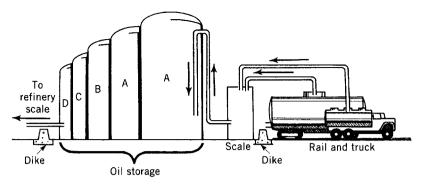


Figure 9. Ideal bulk storage system.

at temperatures conducive for enzymatic and microbial growth, emphasize the importance of removing non-triacylglycerol materials.

Removal of phospholipids is desirable because crude oil stored for extended periods is apt to deposit sludge in the bottoms of storage tanks, barges, or rail tank cars (21). Phospholipids (1-3%) represent the bulk of the fat-soluble materials in most crude vegetable oils and are particularly troublesome with soy oil. Soybean oil is the major commercial source of lecithin.

Storage of crude fats and oils is necessary to maintain sufficient quantities of oil to supply the refining operation. The objectives of such a bulk-storage system are also to maintain the quality of the incoming crude oil and to supply a uniform product to the refining operation (22–24). An ideal bulk-storage system is depicted in Figure 9. Key features include: (1) storage tanks and piping for each type of crude oil to be stored and handled, (2) an inventory control system that allows an accurate measure of crude oil coming into the refinery and to the refining operation, and (3) a spill prevention, containment, and control system. Items (1) and (2) are particularly important in preventing comixing, and mixing of old product with new where the deteriorated one could catalyze oxidation.

2.3. Quality Deterioration During Storage

The most serious types of quality deterioration occurring in bulk storage of crude fats and oils include comixing, contamination, chemical changes, and color increases (22).

Coincidential Comixing. Comixing occurs through the undesired mixing of different types of crude oils and can occur either through human error, faulty equipment design, or both. Comixing can be prevented by separating tanks and piping systems for each major type of crude oil handled. It can also be avoided by using strict operation procedures.

Contamination. Fats and oils with appreciable amounts of phosphatides and other easily hydratable materials, such as those from soybean, cottonseed, corn, rapeseed, etc., can be contaminated with moisture. Conditions of high humidity, warm oil, and cool temperatures can produce sweating within crude oil storage

tanks. In effect, water dripping into the oil causes an in situ degumming of the oil with an accumulation of sludge deposits on the bottom of the tank. The effect can be minimized by employing vent systems that restrict the flow of air in and out of the tank.

In the course of long-term storage, crude oils may be contaminated by oxidized or hardened oils that eventually coat the tank walls as a patch and provide uneven quality deterioration. This can be prevented by periodic cleaning of the tanks.

Chemical Changes. Primary considerations during crude oil storage and handling include preventing hydrolysis and oxidation of the crude oil. Storage of crude oil in the presence of moisture promotes hydrolysis, which, in turn, leads to increases in free fatty acids and lower yields of refined oil. Hydrolysis can be best prevented by ensuring that tanks are completely dry prior to pumping crude oil into storage and by keeping the oil as cool as possible throughout all handling operations.

Oxidation of crude oil may be prevented by excluding oxygen and air from the oil. One way is to fill storage tanks from the bottom, thereby minimizing exposure to the air as it enters the tank. A second, but more expensive, way to preserve crude oil quality is to blanket storage tanks with an inert gas such as nitrogen. However, inert gas blanketing is generally used more in conjunction with finished oil storage and handling. These techniques will be discussed in detail later.

Trace metals, in particular iron, copper, and nickel, accelerate the oxidative deterioration of fats and oils. Crude oil should not be in contact with iron, copper, or brass valves. One brass valve in a soybean oil refinery can lower the flavor stability of deodorized products. For proper handling, only stainless-steel tanks and valves should be used.

Color Fixation. Oxidation of crude fats and oils can also lead to *color fixation*. The most notable examples of color fixation are in cottonseed (25) and palm oils, where oxidation of gossypol and carotenoid pigments are involved.

Although not particularly sensitive to color fixation, the lecithin in crude soybean oil may darken excessively if the oil needs to be melted prior to unloading from rail tank cars or trucks. The use of high-pressure steam on heating coils should be avoided. Instead, low-pressure steam or, better yet, hot water should be used for this purpose. It is highly advisable to use longer time in slow and mild heating in order to give a gentle treatment to the oil in qusetion.

2.4. Equipment for Storage and Handling of Crude Fats and Oils

Tanks. Crude oil storage tanks are usually constructed of welded iron, aluminium, or stainless steel. Their sizes vary throughout the industry depending on the refining capacity of the particular plant and the availability of incoming crude oil. Storage tanks with a capacity of 446,000 kg (1 million pounds) are not uncommon.

Crude oil storage tanks may be located in the open or in an enclosed area. If located outside, they should be set on concrete pads to protect them from surface water that eventually can cause rust and corrosion (26). A practical method for protecting crude oil quality involves painting outside storage tanks with aluminum or

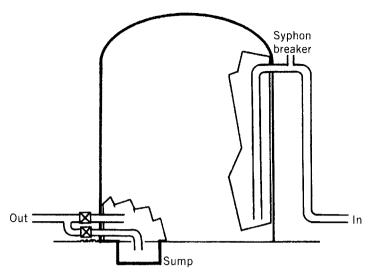


Figure 10. Typical piping arrangement for a crude oil storage tank.

white paint. Such tanks may be as much as 11 °C (51.8 °F) cooler than those painted black (27). Most vegetable oils will not usually freeze in cold weather when held in large storage tanks. However, because storage tanks may be used for harder oils with higher melting points, the tanks should be equipped with heating coils to facilitate melting of bulk-stored fats and oils when required. We very highly recommend only stainless-steel tanks, as this investment will payoff in long run due to the absence of any variance in quality. These tanks should be built with nitrogen facility so that the oil is always protected under an invert atmosphere.

Successful refining is, in part, dependent on the supply of uniform crude fats and oils to the operation. Thus, storage tanks for crude fats and oils should be equipped with agitators to allow blending of crude oils and to assure uniformity.

Typical piping arrangement for a crude oil storage tank is depicted in Figure 10. Key features include an inverted U-shaped piping arrangement with a syphon breaker at the top. This lessens the possibility of oil in a full tank accidentally flowing to a tank containing less oil; also, it permits filling a tank from the bottom, thereby minimizing exposure of the oil to air. The storage tank can be emptied through one of two outlets: one is a short distance off the bottom and the second is from the sump. This arrangement allows any foreign material to settle to the bottom where it will not be picked up, and the tank can be cleaned by using the sump outlet (22).

2.5. Unit-Processing Operations

The purpose of this section is to outline the basic unit-processing operations required to convert crude fats and oils into finished products, such as cooking-salad oils, margarine, and shortening base stocks. Edible fats and oils are handled within

the unit-processing operation by pumping them through pipes. All edible fat and oil processing steps consist of independent operations that are usually not connected with each other by continuous flow. Between each processing step there may be one or more storage tanks. Generally, in each processing step, the oil is heated to process temperature, held for reaction, and cooled to preserve oil quality. Between processing steps, the oil is allowed to cool to a minimum or ambient temperature while being maintained in a fluid state to facilitate material handling by pumping (28).

The basic processing steps consist of (1) crude oil storage (2) degumming or caustic refining (3) bleaching (4) hydrogenation (5) fractionation or winterization (6) deodorization and (7) finished oil storage. Each step removes specific components from the oil. These materials may be classified as:

- 1. *Naturally occurring*: gums, phospholipids, pro-oxidant metals, pigments, color bodies, tocopherols, free fatty acids, and diacyglycerols
- 2. New compounds formed during processing: soaps, oxidation products (primary hydroperoxides and secondary decomposition products), polymers and their decomposition products, color bodies, triacylglycerol and diacylglycerol isomers, high-melting triacylglycerol, and *trans*-fatty acids
- 3. *Processing adjuncts*: hydrogenation catalysts, bleaching clay, metal scavengers that precipitate from finished oils, i.e., citric acid
- 4. *Contaminants introduced by processing*: moisture, trace metals, carbonaceous materials, and oil-insoluble materials

To produce an edible fat (an oil having the desired color, flavor and oxidative stability, and functional properties), naturally occurring and undesired compounds must be removed as efficiently as possible, with maximally preventing damage to the naturally occurring antioxidants and neutral oil fraction. Formation of new compounds, precipitated processing adjuncts, and contaminants are all undesirable.

A summary of typical handling operations and storage conditions for edible fats and oil products within the unit operations is shown in Table 4.

Virtually all edible fats and oils exhibit the best oxidative stability in their crude state. With increased processing, oxidative stability decreases and reaches a minimum after bleaching. Refined-bleached oil is the least stable, and extended storage of this oil is not desirable. Deodorization and treatment of the oil with metal inactivators or autioxidants cannot be relied on to correct faulty upstream handling and processing as peroxide buildup during crude oil storage, degumming, refining, or bleaching will ultimately have a detrimental effect on the storage properties of the finished oil. Storage and handling practices should be designed to compensate for the decreased oxidative stability.

2.6. Finished Oil

A review of finished-oil handling and storage in the industrial trade sector has been given by List and Erickson (31). For reviews of finished-oil handling and storage

TABLE 4. Storage and Handling of Soybean Oil within the Unit-Processing Operations (23, 24, 26, 29, 30).

Unit Processing Operation	Substance(s) Removed	Handling Operation(s)	Process Reaction Temperature °C (°F)	Oil Storage Temperature °C (°F)	Atmosphere
Crude oil storage	Oil insolubles	Pumping: tank cars, trucks, or barges to storage tanks	Ambient to 54 (130)	Ambient	Air
Degumming	Phosphatides Trace metals	Pumping: Storage tank to mix tank to centrifuge to storage or refining	70 (158)	Ambient	Air
Caustic refining	Free fatty acids Phospholipids Trace metals Pigments—color bodies	Pumping: Storage tank to inline mixer to centrifuge	74 (165)	Ambient to 50 (122)	Nitrogen or air
Water washing	Soaps	Pumping: From primary centrifuge to water wash centrifuge	88 (190)	Ambient to 50 (122)	Nitrogen or air
Drying	Moisture	Pumping: From water wash centrifuge to vacuum dryer to storage tank	82 (180)	Ambient to 50 (122)	Nitrogen or air
Bleaching	Pigments, soaps	Pumping: Storage tank to bleaching unit to filter to storage tank	105 (224)	Ambient to 60 (140)	Nitrogen or air
Hydrogenation	Olefinic bonds	Pumping from storage tank to hydrogenation converter	140–225 (284–437)	Approx. 10°C (180°F) above melting point	Nitrogen or air
Winterization	High melting triacylglycerols and waxes	Pumping from converter to chill tank through filter	4–5 (30–35)	60–66 (140–151)	Nitrogen or air
Filtration	Spent bleaching clay	Pumping from converter to filter to storage tank	4–5 (30–35)	Ambient to 60 (140)	Nitrogen or air
Deodorization	Pigments Unsaponifiables Free fatty acids Odor and flavor compounds	Pumping from storage tank to deodorizer	204–274 (400–525)	60–66 (140–151)	Nitrogen or air
Polishing filtration	Bleaching earth Citric acid Carbonaceous material	Pumping from deodorizer to polish filter to oil cooler to storage tank	50–70 (122–158)	60–66 (140–151)	Nitrogen or air
Finished oil storage	Oil insolubles	Pumping from storage tank to polish filter to packaging line or to tank cars or tank trucks	33 73 (122 133)	60–66 (140–151)	Nitrogen or air

within domestic and European refineries, articles by Wright (29) and Johansson (30) should be consulted. Weiss (32) has reviewed the bulk handling of shortening in the industrial and institutional sectors.

A finished oil is defined as that fat or oil product ready for use alone or as an ingredient without further processing. Assuming that raw materials are of high quality and previous operations are satisfactory, the result is a light-colored product, free from odors, flavors, hydroperoxides, and contaminants. The goal of finished-oil storage and handling is to preserve and maintain these quality factors (33).

A general scheme for the storage and handling of finished oils is shown in Figure 11. Oil coming from the deodorizer is passed through a heat exchanger and a polishing filter to remove any solid materials. After the polishing filtration, the oil is pumped through a cooler to a storage tank. Before packaging, the oil is generally filtered again to remove any solids picked up while in storage. Paper is generally used for this filtration (29).

Autoxidation increases markedly with temperature. Salad oils degrade rather quickly with increasing temperatures due to their high unsaturation. From this standpoint, it is desirable to handle the oil at temperatures as low as possible during discharge from the deodorizer into the storage tank. In practice, however, it is not desirable to cool the oil below 45 °C (113 °F) prior to the polish filtration for the following reasons: (1) moisture is apt to condense in the oil and (2) at lower temperatures the filtration rate decreases.

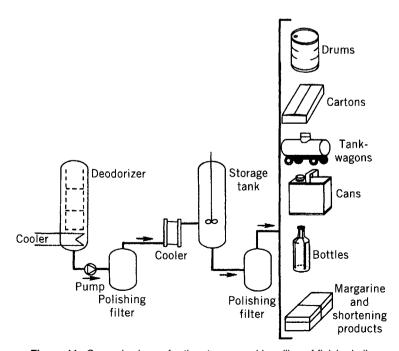


Figure 11. General scheme for the storage and handling of finished oils.

Further cooling before storage is generally considered optional. Where storage tanks are not blanketed with nitrogen, cooling is desirable. On the other hand, the use of nitrogen-gas blanketing may eliminate the need for cooling.

2.7. Storage Tanks for Finished Products

Storage tanks for finished fats and oils are preferably constructed of carbon steel, stainless steel, or aluminum. Finished-oil storage tanks vary considerably in size. Typically, they are designed to hold a given number of standard rail tank carloads of oil or a full operation batch of a deodorization vessel. A tank holding 500 metric tons of product is considered large, and a 10-metric-ton tank is considered small.

Finished-product storage tanks are usually closed and fitted with tank tops, internal heating or cooling coils, and an agitator to promote heat transfer and to prevent localized overheating. A typical finished-product storage is depicted in Figure 12.

Factors most likely to affect the quality of finished products to such an extent that they would require reprocessing or use as a subquality product include: (1) contamination from atmospheric adulterants, (2) internal contamination from water and soaps, (3) overheating, and (4) exposure to air and oxygen. Atmospheric adulteration is avoided by storing the product in completely closed tanks. Finished products held in storage tanks can be contaminated by water leaking from steam or cooling coils. Moisture in the oil can promote hydrolysis, particularly at elevated storage

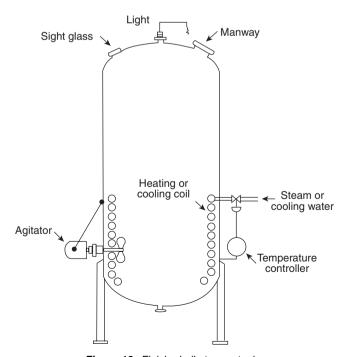


Figure 12. Finished-oil storage tanks.

temperatures. Properly maintained coils are necessary. Overheating of bulk-stored oil is undesirable because soaps and pro-oxidant metals are much more active at elevated temperatures (34, 35). Finished-oil storage tanks are equipped with automatic temperature controllers to prevent overheating (Figure 12) (29).

2.8. Nitrogen Blanketing

Oxidation has the most detrimental effect on the quality of finished products held in bulk storage. Thus, exclusion of oxygen during storage represents a highly desirable and practical method for preventing quality deteriorations (29, 36–38).

The usual procedure involves replacing air with nitrogen. Finished product is delivered from the deodorizer to the storage tank under a complete nitrogen blanket. Nitrogen can be supplied from a tank of liquid nitrogen or from commercially available nitrogen generators. Liquid nitrogen is distributed at a purity of 99.998%, in capacities of 1890–340,000 L (500–90,000 gal; 46,600–8,400,000 ft³). The tanks can be equipped for either gaseous or liquid withdrawal. For gaseous applications, a line of vaporizers—atmospheric, electric, steam, or hybrids—can be used to convert the liquid to gas, which is then discharged at the required pressure to use points.

Users of very large quantities of high-purity nitrogen [405,145 L (107,181 gal; 10,000,000 ft³) per month or more] can employ a cryogenic system, an air-separation system designed to filter, compress, purify, and liquefy intake air from the surrounding environment. Nitrogen is recovered from the liquefied air by fractional distillation. These systems range in capacities of less than 608 L (161 gal; 15,000 ft³) per hour to more than 12,154 L (3215 gal; 300,000 ft³) per hour at purities of 99.999% nitrogen or higher.

A self-contained, skid-mounted membrane air-separation system is commercially available that generates nitrogen at flow rates of up to 2431 L (643 gal; 60,000 ft³) per hour, at pressures up to 10.5 kg/m² (150 psig), and at purities ranging from 95% to 99.95%. The membrane systems are based on the selective permeability of the composite membrane fiber. Intake air is filtered, compressed, and cooled before entering the air-separation modules under pressure. Relative to oxygen, carbon dioxide, and water vapor, nitrogen does not readily permeate the composite membrane fiber and flows automatically into the pipeline distribution system at the specified volume, pressure, and purity.

A third method of on-site generation of nitrogen is the vacuum-pressure swing-adsorption process designed to separate nitrogen from air and generate between 405 L and 2026 L (107 gal and 536 gal; 10,000 ft³ and 50,000 ft³) per hour at purities between 99.0% and 99.9% or higher. Offered as a skid-mounted system, a vacuum-pressure cycle combined with adsorbent vessels packed with synthetic zeolites cycle automatically to provide a continuous flow of nitrogen; while one vessel is purifying nitrogen to specifications, another is being regenerated. When intake air enters the active adsorbent vessel, the adsorbent selectively separates oxygen from nitrogen, which is produced to the specified flow and pressure.

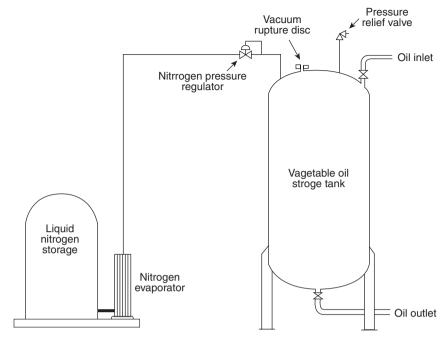


Figure 13. Simple nitrogen-blanketing system.

Generally, these on-site methods are more cost effective than liquid nitrogen for purities lower than 99.5%; however, too low a nitrogen purity may lead to problems with stability of vegetable oils.

A simple nitrogen-blanketing system is shown in Figure 13. The nitrogen blanket is maintained by a pressure system controlled by a regulator. As the tank is filled with product, the pressure builds and the gas is vented to the atmosphere. Conversely, as the product is pumped from the tank, the pressure drops and replacement nitrogen gas enters the tank. It is common practice to equip storage tanks with a vacuum-relief valve or with rupture discs that prevent a vacuum and subsequent collapse of the tank. Nitrogen blanketing can be applied to multitank arrangements (Figure 14). The design is similar to single-tank systems and has the advantage of being less wasteful of nitrogen; as one tank is emptied, the gas can be displaced from another. When product is transferred from tank to tank, the inert gas is merely exchanged. Nitrogen pressures in such systems are kept at 1-15 psi. During filling or emptying, the pressures vary, but relief valves are set to release at pressures above 15 psi. Nitrogen-blanketed storage tanks will not support life and should be thoroughly purged before maintenance personnel attempt to enter the tanks. Signs warning of this hazard are normally displayed on nitrogen-blanketed tanks (29).

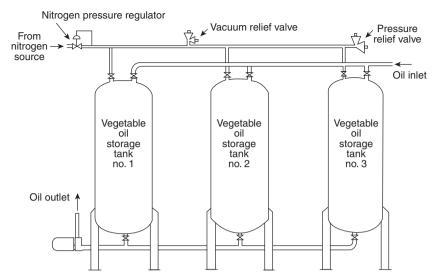


Figure 14. Multitank nitrogen-blanketing system.

2.9. The Industrial User Sector

Industrial users of fats and oils, such as those involved in the manufacture of fried foods and baked goods, often purchase their supplies in bulk because of cost advantages. Among these are elimination of cost of shipping containers, reduced shipping rates, and reduced labor costs due to more efficient unloading and handling of products within the user's plant. Other advantages include reduction in product waste and sanitary problems associated with small containers. Bulk handling also may reduce the amount of storage space needed, and this factor can be of economic importance in some plants.

On the other hand, bulk handling offers some disadvantages, including sizable capital investment for the purchase and installation of pumps, tanks, and other essential equipment. Operation of a bulk-handling system requires the attention of more skilled personnel than the simple unloading and handling of smaller containers. Another disadvantage is that the product may deteriorate before being used. This is particularly true of shortenings that must be held in a molten state. Melted products are generally more susceptible to deterioration than packaged semisolid products.

A prime requirement is that a minimum shipment, usually 13,392 kg (30,000 lb), be used within the storage life of the product. The storage life of shortenings varies with formulation, and the storage and handling conditions vary within the user's plant. Suppliers should be consulted to determine the storage life of shortening products.

Many types of fats and oils are amenable to bulk handling, including all salad and cooking oils, all types of frying fats, bread shortenings, and products normally fluid and pumpable at ordinary temperatures, such as "fluid" bread and cake

shortenings. Several types of products are not amenable to bulk handling because their physical or functional properties are dependent on proper plasticizing and tempering, and resultant crystal structure are altered by heat or melting. These include: (1) margarines and water–shortening emulsions that will breakdown under heat, with a separation of the fat and water phases, (2) baking shortenings used in the manufacture of cakes and icings, (3) shortenings containing significant amounts of lecithin, and (4) shortenings used in Danish pastry.

2.10. Equipment for Bulk Storage and Handling

Equipment required for bulk handling include: (1) tank cars or tank trucks and isotankers for transporting bulk shipments, (2) equipment for unloading the fats, (3) storage tanks, and (4) equipment necessary to deliver the product to the point of use within the user's plant.

Rail tank cars are rented by the supplier from companies leasing this type of equipment because railroads do not own or furnish equipment to haul liquid commodities such as fats and oils. An advantage of this arrangement is that the shipper of fat products can control the suitability, availability, and utilization of tank cars used for loading of products.

Equipment for Unloading Tank Cars and Tank Trucks. The unloading of tank cars, isotankers, or trucks requires fittings and adapters to connect the unloading line to the tank car, isotanker, or tank outlet. Tank cars generally require 10 cm (4-inch) outlets, whereas 7.6 cm (3-inch) outlets are standard for tank trucks. Flexible hoses made from carbon steel, neoprene, plastic, aluminum, or stainless steel (types 302, 303, 316) are suitable.

A basket strainer should be installed ahead of the pump to prevent damage from tramp metal. In addition, it is recommended that a filter be installed on the pump discharge to remove extraneous materials. In cases where it becomes necessary to pump partially solidified fats, the filter should be installed in such a way that it may be bypassed.

Excellent reviews of pumps for the edible oil industry have been published (39–42). Either centrifugal or positive-displacement pumps may be used, but the latter are preferable. Pumps should be constructed of carbon steel or stainless steel and have sufficient capacity to unload a 32,280-L (8000-gal) tank car in about 2 h or less. Factors governing pump selection include length of lines; restrictions, such as elbows and valves in the lines; height to which the fat must be pumped; type and temperature of fat being pumped; and whether the pump is located above or below the fat level in the storage tank. A relief valve must be installed to prevent damage to positive-displacement pumps in the event the discharge becomes blocked. Centrifugal pumps, however, do not require relief valves.

Certain utilities are required to unload liquid fats. These include pressurized air or nitrogen for clearing the connecting line and hot water or steam for melting solidified fats. It is also advisable to insulate the unloading lines, even if the shipment is hot and liquid on arrival. A drain valve should be installed at the lowest point in the line to prevent accumulation of fats, which can solidify and cause a blockage.

Tank cars require a level surface for unloading. However, complete unloading of tank trucks may require a slope toward the unloading end. The area underneath should be concrete and pitched toward a drain to receive wash water and maintain good sanitation.

Sparging Techniques. Sparging and nitrogen-blanketing techniques for protecting edible oils during truck and rail car shipments have been reviewed (22, 37). Sparging (Figure 15) represents a practical method for protecting finished oils from oxidative deterioration during shipment from refinery to destination. The technique is particularly useful when finished oils are loaded into tank cars and trucks.

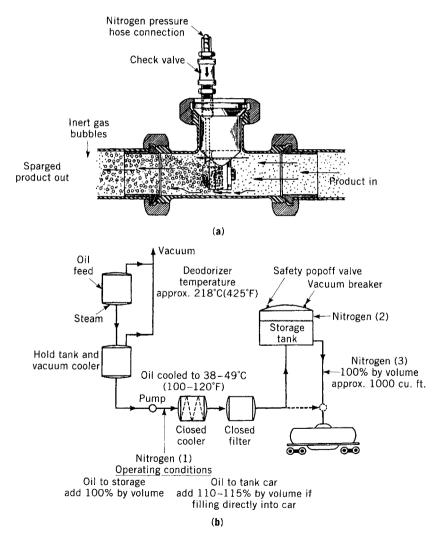


Figure 15. Nitrogen-gas sparger and blanketing system for loading tank cars and trucks: (a) inline sparger and (b) complete system.

The principle involved is saturation of the oil with nitrogen while it is completely free of air and oxygen. A sparger introduces minute bubbles of nitrogen into the oil stream; as the saturated oil falls into the tank car or truck, the effusing gas sweeps the headspace and, thus, removes most of the air and oxygen from the vessel (30). Another benefit of nitrogen sparging is the reduction of oxygen picked up from natural leakage of air into the tank car or truck. The gradual flushing action of the sparge gas reduces the reabsorption of oxygen because of the pressure differential between the liquid and the headspace above it (37). A nitrogen gas sparger and blanketing system for loading tank cars and trucks is illustrated in Figure 15. Nitrogen blanketing and sparging techniques have many other applications in protecting oil quality. A summary is given in Table 5.

2.11. Precautionary Measures in Bulk Handling

In bulk-storage systems where positive-displacement pumps are used, special precautions are necessary on both sides of the pump. On the suction side, a doubleside, double-check system should be used to avoid pumping the fat from a closed vessel, thereby preventing collapse of the tank and piping. Similarly, on the discharge side, checking for closed valves or relief valves is recommended to prevent danger to operating personnel, damage to equipment, and loss of product from blown fittings.

When it is necessary to heat fats to keep them fluid, heat should be applied to line, pumps, and tanks. Although insulation may be used to retain the necessary amount of heat, the ability to apply heat in emergency situations is most desirable. Occasionally, even when shortenings are held above their apparent melting point, hard fractions will separate or "seed" out or fractionation will take place. In effect, the composition of the fat changes in different levels in the tank and possibly can block the lines. Application of heat and agitation may be necessary to correct the problem. It is recommended that experimentation on the product be carried out at the projected temperatures and times to ensure that this problem will not occur under operating conditions in the plant.

Close control of temperature within handling systems is necessary because pumping rates are dependent on viscosity of the fat, which, in turn, is temperature dependent. Similarly, where volumetric means are used to control weights, it is absolutely essential to control temperature because the specific gravity is related to temperature. Graphs showing these relationships have been published by Erickson (33).

Cleaning procedures for bulk storage and handling systems are beyond the scope of this chapter. For a thorough discussion of this topic, the reader is referred to List and Erickson (31).

2.12. Packing of Institutional Shortenings and Margarines

Industrial and commercial shortenings are packaged in 2.3-kg (5-lb) prints packed in 22.7-kg (50-lb) case, 22.7-kg (50-lb) plastic pails and cubes, 172.4-kg (380-lb)

TABLE 5. Summary of Treatment Areas with Nitrogen to Protect Edible Oils (37).

Area of Treatment	Method of Introducing Nitrogen	Classification	Approximate Usage (ft ³)
Manufacturing pumping from deodorizer	In-line between cooler and storage tank	Sparging	Approx. 0.125 ft ³ /gal
Bulk oil storage	From sparger directly into headspace	Blanketing	Enough to maintain positive pressure
Filling of tank cars	In-line between storage and tank car	Sparging	1000 ft ³ /8,000-gal car
Tank car or truck	Into headspace	Blanketing	Undetermined filling
Customer's plant pumping from tank car to oil storage	Sparging in-line during pumping	Sparging	Approx. 0.125 ft ³ /gal
Storage in tanks	Directly into headspace plus nitrogen from sparger	Blanketing	Enough to maintain positive pressure
Pumping from storage to filler or header	Sparging in-line during pumping	Sparging	Approx. 0.125 ft ³ /gal
Filler bowl or header	Entrance into closed filler bowl or header pressure	Blanketing	Maintain slight positive pressure
Closing or capping machine	Shroud or purge technique	Blanketing or purging	Undetermined

open-end steel drums, or 907.2-kg (2000-lb) totes. Although attractiveness is not ignored, it is secondary to cost, protection, and convenience (32). Friction-top pails are convenient when only a part of the contents are used at one time because they are easy to reclose and store. The empty pails can be used for other purposes in the kitchen or bakery. Commercial shortenings are also packaged in corrugated paper boxes measuring about 30.5 cm (1 ft) on a side. Polyethylene film is used to line the box and prevent leakage. This type of packaging is popular because it is cheap, the contents are easily removed, and the package can be readily disposed of by folding flat. Storage problems are minimal because the package takes up little space. Plastic cube liners are usually colored because they melt in hot fat if they are accidentally dropped into a fryer, and the color makes them easy to detect and retrieve. A potential disadvantage of cube packaging is that melted cube liners cause foaming, darkening, and smoking of the frying fat (32).

Drum-packaged pourable shortenings may be emptied upright with a hand-operated pump or emptied by gravity through a spigot with the drum placed horizontally on a rack. Similarly, totes may be pumped or emptied by gravity from a valve and hose connection.

Fully hardened fats are sold as flakes or powdered materials and are packaged in multiwalled paper bags holding 22.3 kg (50 lb), in fiber drums holding 44.6–89.2 kg (100–200 lb), or larger bulk containers.

Margarines intended for institutional and industrial trade are often packaged in pails holding 13.4–22.3 kg (30–50 lb) and in cubes. Open-end steel drums [208.7 L (65 gal)] hold 181.5 kg (400 lb) of margarine. It may also be available in 2.3-kg (5-lb) prints or sheets packed in 22.7-kg (50-lb) box.

2.13. Storage of Shortenings Effect on Functional Properties

Excellent discussions of shortenings are given by Weiss (32), Hartnett (43), and Thomas (44); these should be consulted for information on formulation, processing, and end uses. Shortenings may be classified as solid, fluid, liquid, and powdered. Five factors govern the quality of shortenings: (1) triacylglycerols and emulsifier composition (2) processing conditions (3) tempering conditions (4) usage temperature and (5) storage conditions.

Solid Shortenings. Solid shortenings are the most generally useful products of their class because they may be used for both frying and baking. The crystal structure is an important consideration in solid shortening compositions. For example, for optimum creaming ability (or the ability to incorporate air into a cake batter), the shortening must be stable and in the β' form and characterized as being smooth and creamy. These products can be adversely affected by improper and nonuniform storage conditions. As reflected by pound cake volume, general-purpose solid shortenings will show no loss in creaming ability over storage temperatures of 4.4–21.1 °C (40–70 °F). Beyond that, a marked loss of creaming ability is observed. Prolonged storage of solid shortenings at high temperatures causes the lower melting-fat fractions to liquefy; upon cooling, they solidify into crystal forms that are less functional (43).

Solid shortenings require no refrigeration during storage. However, they will absorb odor. They should be stored in a cool, dry place away from odor-producing materials.

Fluid Shortenings. Fluid shortenings are pourable, opaque products containing suspended solids that are hardfats or emulsifiers, depending on whether the product is to be used for frying or baking. Like solid shortenings, proper storage temperatures are important in preserving the functional properties of the product. Storage of fluid shortenings at temperatures below 18.3 °C (65 °F) will cause the product to set up and lose fluidity. Loss of fluidity can be reversed by mild warming. Storage at temperatures beyond 35 °C (95 °F) will cause either partial or complete melting of the suspended solids. This, however, is not a reversible phenomenon because cooling will cause formation of large crystals that will not remain in suspension. If the product is formulated with hardfats as the suspended solids, improper storage might be of little consequence because they will merely settle to the bottom of the container upon cooling. On the other hand, if the solids are emulsifiers, settling out will upset the balance of the product, with the upper portion under-emulsified and the bottom part over-emulsified. Thus, the product would not perform as intended (32).

Liquid Shortening. The liquid shortenings include regular cooking oils, salad oils, and products resulting from fractionation of semi-hardfat. These products are not ordinarily emulsified. Ordinary cooking and salad oils pose no unusual storage problems because they possess no crystal structure to protect and have no suspended solids. If they are stored at temperatures low enough to cause solidification, they can easily be returned to clear liquids by returning the product to ambient storage conditions.

2.14. Factors that Contribute to Oxidative Deterioration of Finished Products

The concept and discussion of atmospheric oxidation were introduced earlier. As a result of the importance of preventing oxidation in finished products, a more thorough discussion follows. It should be pointed out that the effects of atmospheric oxidation apply to all fats and oils regardless of their stage of processing.

Five factors contribute to the oxidative deterioration of fats and oils: (1) oxygen or air (2) heat (3) light (4) pro-oxidant metals and (5) time.

Although the elimination of air prevents oxidative deterioration, complete elimination of air is impractical. The solubility of oxygen in soybean oil is quite high (2.1 mL/100 mL) at 22–23 °C (45) and is sufficiently soluble to yield a peroxide value of 18 (46), assuming complete reaction. Flavor deterioration in soybean oil occurs at peroxide values considerably lower than 18. Published data show that soybean oil can have poor flavor at a peroxide value of 1 (47).

Even when using nitrogen blanketing, sufficient oxygen already may be present in the oil to promote oxidative deterioration (see section on sparging). A more practical approach is to minimize the incorporation of air into the oil by proper handling procedures.

Faulty handling procedures to be avoided are as follows:

- Allowing a liquid fat to cascade or fall through air into storage or holding tanks. As mentioned previously for crude fat and oil handling, a more desirable procedure is to fill the tank from the bottom with subsurface entry.
- 2. Sucking of air into the suction side of pumps or lines caused by faulty pump seals or fittings.
- 3. Whipping air into a fat through improper agitation within storage tanks. Creation of whirlpools or vortexes should be avoided.
- 4. Minimize blowing of lines with air, which in turn may bubble air through the fat being held in the storage tank.

Heat accelerates the reaction of atmospheric oxygen with edible oils. For deodorized products, it is estimated that the speed of oxidation is doubled for each 15 °C (59 °F) increase in temperature over the range 20–60 °C (68–140 °F) (31). A rule of thumb for handling is to keep the fat no warmer than necessary to facilitate handling by pumping. For hydrogenated fats, a holding temperature 5.6 °C (10 °F) above the melting point is considered sufficient. Design of bulk-storage systems should take into account the use of low temperature whenever possible. For example, short insulated lines will permit lower storage temperatures and, thus, prolong the quality of bulk-stored fats.

Localized overheating is detrimental to fat quality and should be avoided. All storage tanks with heating devices should be equipped with a mechanical agitator. Power agitation will not only minimize fat damage from localized overheating but will save time and heating costs as well. If agitation is temporarily out of service, the temperature differential between the fat and the heating medium must be kept minimal.

All edible fats and oils deteriorate under the effects of light. Normally, light-induced deterioration is not of concern in the oil-processing operation or at the user level because processing, handling, and storage are carried out within closed systems. However, light deterioration is an important factor in the storage stability of liquid oils packaged for retail trade.

The importance of avoiding metallic contamination cannot be overstressed. Copper and iron are strong pro-oxidants capable of lowering the flavor and oxidative stability for fats and oils at levels of 0.01 ppm and 0.1 ppm, respectively (48). Copper or copper-containing alloys should never be used in equipment used for handling and storing fats and oils. The prevention of iron contamination is somewhat more difficult, because most of the industry uses black iron for construction of tanks, pumps, and lines. However, through proper treatment and cleaning of black iron equipment, iron contamination can be kept to a minimum.

Any fat or oil will deteriorate with prolonged time even if stored and handled under ideal conditions. Unhydrogenated or lightly hydrogenated oils, which do not require heat for keeping them liquid, have greater resistance to deterioration than do shortenings. The latter, however, will keep for 2–3 weeks in a melted

condition. Shortenings should not be allowed to solidify and then be reheated during use. Bulk-storage systems should be designed with a maximum turnover time of 2–3 weeks or within the storage life of the product. The mixing of fresh shipments with those already in storage should be avoided. Small quantities of old products in a tank may hasten the deterioration of new product mixed with it. Shipments should be scheduled so that mixing of old and new products does not occur. An auxiliary tank can be installed to hold the remainder of the old shipment and permit inspection and cleaning of the receiving tank.

2.15. Transport of Fats and Oils

During transport, the quality of oils may be impacted by oxidation, adulteration from other oils, moisture condensation, contamination with foreign matter (dirt, rust, mould, etc.), and overheating. Transport of fats and oils is designed to preserve quality in the delivery to the product formulator in the most cost-effective manner. The advantages and disadvantages of bulk handling of fats and oils are detailed in Table 6 (33,49). The economics of bulk shipment are the major advantages.

Movement of fats and oils may be as the crude, partially refined, or finished oils and may be by rail tank cars, tank trucks, barges, and tanker ships. Rail tank cars are usually of the standard 60,566-L (16,000-gal; 120,000-lb) or the jumbo 232,170-L (61,333-gal; 460,000-lb) size. Standard cars are designed with a thermal expansion area of about 2% of the total capacity as a dome in the car. However, the rated capacity of the jumbo cars does not include any expansion space. Rather, these cars are equipped with a permanently installed bar marker located in the passageway, above which the quantity of oil should not be loaded. Heating coils can be installed for handling higher melting fats.

Tank trucks typically have 20,412-kg (45,000-lb) capacity. Generally, tank trucks are made of stainless steel but have no standard shape or construction. Heating coils can be installed when carrying oils that might solidify during shipment. Trucks are provided with a bar marker to indicate maximum load level, are insulated, and carry 4.6 m (15 ft) of 7.5 cm (3-inch) hose and the fittings required to unload the oil to a storage tank.

TABLE 6. Bulk Handling of Oils (33, 49).

Advantages	Disadvantages
Container packs unnecessary	Greater capital investment in handling facilities
Lower freight charge per ton	More highly skilled (paid) individual operators
Lower labor handling costs in transit and at destination	A larger quantity purchased at one time
Less loss due to smaller overall holdup in handling facilities (average loss estimated at 0–5%)	Holding time of the commodity is longer and, possibly as a melted solid, places demands on planning
Cost savings in smaller storage area	Bulk shipping requires sanitation and security procedures
No cost for package disposal	

A barge generally has three compartments with a total capacity of 1,270,072 kg (2,800,000 lb). The compartments are fitted with steam coils to melt oils and fats that have solidified during transport. Barges are used to transport crude and crude-degummed oils along major rivers and, in the United States, shipping time is seldom longer than 7–10 days.

Shipment by tanker is the most economical means of ocean transport of fats and oils. A typical shipment ranges from 1814 to 9072 metric tons (2000 to 10,000 short tons). Tankers are compartmentalized and inert-gas blanketing or sparging is not employed because the gas can escape. Rather, the compartments are filled to capacity to minimize headspace air and reduce oxidative deterioration. Heating is not required to unload liquid oils, but to facilitate unloading of palm, coconut, and tallow, heating is required.

Centrifugal pumps with capacities of up to 794,934 L/h (210,000 gal/h) are used for handling nonsettling fats and oils. Positive-displacement pumps are preferred for unloading crude and degummed oils because they will maintain their prime during the operation, which requires an operator to squeegee the remaining foots oils to the tank outlet during the final pumping. Both types of pumps are used to load tankers.

2.16. Temperatures during Shipment and Unloading of Fats and Oils

Extremes of temperature of an oil during shipment can have a deleterious effect on quality because oxidative deterioration and hydrolysis are accelerated by temperature. The International Association of Seed Crushers has established recommended safe limits of temperature during the voyage and on discharge for the principal oils in transport (Table 7) (50).

TABLE 7. Recommended Temperatures (*C): Principal Oils (50).				
Oil	During Voyage		On Discharge	
	Min.	Max.	Min.	Max.
Sunflower	Ambient	Ambient	Ambient	20
Soybean	Ambient	Ambient	20	25
Safflower	Ambient	Ambient	Ambient	25
Peanut	Ambient	Ambient	20	25
Rapeseed	Ambient	Ambient	Ambient	20
Maize	Ambient	Ambient	Ambient	20
Palm	32	40	50	55
Palm stearine (RBD)	40	45	60	65
Palm olein (RBD)	25	30	50	55
Coconut	27	32	40	45
Fish	20	25	30	35
Palm fatty acid distillate	42	50	67	72

TABLE 7. Recommended Temperatures (°C): Principal Oils (50).

2.17. International Codes and Previous Cargo Listing for Shipment of Fats and Oils

During recent years, international fats and oils associations and the Fats and Oils Committee, Codex Alimentarius, have been quite concerned about previous cargos carried in tankers for shipment of edible oils. A listing of acceptable previous cargos has been promulgated by the Federation of Oils, Seeds and Fats Associations (FOSFA) (51). This information is also available from NIOP (National Institute of Oilseed Products), a U.S. association. The listing includes five generic items that greatly extend the coverage of the list: acid oils and fatty acid distillates; animal, marine, and vegetable oils, other than cashew shell nut oil and tall oil; beverages; dairy products; and fatty acid esters. The same organization has assembled a list of 42 items banned as immediate previous cargos, including isocyanates, phthalates, transformer oils of the PCB type, lube oil additives, uncured epoxy resins, and all leaded products (52). Another concern has been the establishment of a standard reference document concerning advice on the storage and transport of edible oils. Such a document has been developed under the leadership of the Malaysian Palm Oil Board (MPOB) and adopted as an international code of practice by Codex Alimentarius (53, 54). Advice is given on storage tanks and ship's tanks, pipelines, heating, loading, unloading, and cleaning.

2.18. Oil Spill

Under Section 311 of the Clean Water Act, the U.S. EPA amended the Facility Response Plan requirements in the Oil Pollution Prevention regulation for nontransportation-related facilities. The main purpose of these amendments is to provide a more specific method to plan response resources that can be used by an owner or operator of a facility that handles, stores, or transports animal fats and vegetable oils. EPA issued this rule in response to legislation requiring the Agency to issue regulations (55).

Spill-prevention procedure is beyond the scope of this chapter. For a thorough discussion of this topic, the reader is referred to List and Erickson (31).

3. DETERIORATION PROCESSES

3.1. Oxidative Deterioration During Long-Term Storage

Significant amount of knowledge of oxidative and related forms of deterioration occurring in long-term storage of soybean and cottonseed oil (56) was obtained from studies conducted at the U.S. Department of Agriculture (57–61) between the late 50s to the early 70s. A most interesting and informative study reported the oxidative stability of soybean oil at various processing stages, and the results were related to commercial storage conditions (38). As oxidative deterioration is an important consideration in the processing, storage, and handling of soybean and other oils, these studies are reviewed briefly here.

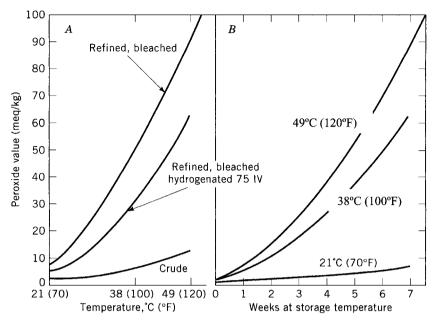


Figure 16. Effects of processing and storage temperature on oxidative stability as measured by peroxide value. (A) 1-qt container held for 7 weeks in storage. (B) Refined and bleached oil in 1-qt size container.

Effects of Processing and Storage Temperature (38). A fresh, non-degummed soybean oil was refined, bleached, and hydrogenated to an iodine value of 75. Samples from each processing stage were placed in closed 0.946-L (1-qt), 22.3-kg (50-1b), and 208.2-L (55-gal) containers and stored at 21.1 °C, 37.8 °C, and 48.9 °C (70 °F, 100 °F, and 120 °F). The effects of processing and storage temperature on oxidative stability as measured by peroxide value are depicted in Figure 16, parts A and B, respectively.

Part A [0.946-L (1-qt), samples] shows crude oil to be most stable; refined and bleached are most prone to develop peroxides under accelerated storage conditions. Part B shows the marked effect of temperature on peroxide development in refined, bleached oil. Peroxides developed very slowly at 21.1 °C (70 °F) but increased markedly at 37.8 °C (100 °F), and 48.9 °C (120 °F), probably because oxygen diffuses more rapidly into the reaction interface at higher temperatures. The oxidation rate doubles for every 11.1 °C (20 °F) increase in temperature.

The effect of container size on the oxidative deterioration of refined, bleached soybean oil stored at 48.9 °C (120 °F) for 5 weeks is shown in Figure 17. The results clearly demonstrate that oxidation is not only a function of time and temperature but also of the surface area. Figure 17 shows that as the container size increases, the surface-to-volume ratio decreases and peroxide development is an approximately linear function of surface-to-volume ratio.

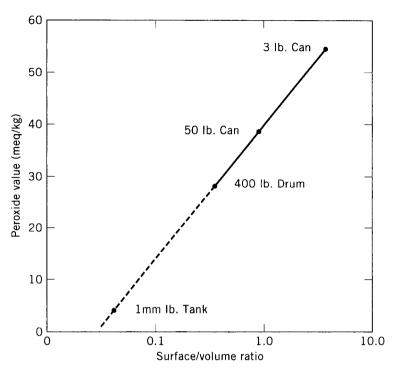


Figure 17. Effect of container size on the oxidative deterioration of refined, bleached soybean oil stored at 49°C for 5 weeks.

Extrapolation of the laboratory data to a storage tank of 9.2 m (30 ft) in diameter with an oil capacity of 453,597 kg (1 million pounds) would predict that the refined, bleached soybean oil would reach a peroxide value of 3.5 after 5 weeks storage at 48.9 °C (120 °F). However, laboratory conditions are seldom, if ever, duplicated in commercial storage tanks. For example, under constant-temperature conditions in the laboratory, little or no oil movement results from temperature gradients. However, field storage tanks are subjected to continual day and night conditions that cause development of sizable temperature gradients and produce considerable internal oil movement. Such movement would be expected to increase the quantity of oil available at the surface and to accelerate oxygen diffusion. Thus, the rate of oxidation in field storage tanks would be somewhat faster than at similar temperatures in the laboratory.

Attempts were made to relate the laboratory studies to commercial practice (38). Refined, bleached soybean oil (1.5 million lb) was thoroughly mixed in a nitrogen-blanketed tank, after which one-half was moved to an air-blanketed tank. Storage conditions are given in Table 8. The two half-filled tanks, one blanketed with air and the other with nitrogen, were stored at ambient conditions for 5 months, after which samples were hydrogenated, deodorized, and subjected to organoleptic evaluations. Flavor stability also was determined on the pilot-plant-produced shortening stock made from the two lots of stored oil.

Conditions	Nitrogen	Air
Oil temperature		
Range	15.6-33.9 °C (60-93 °F)	17.8-30.6 °C (64-78 °F)
Average	23.9°C (75.0°F)	23.9 °C (75.0 °F)
Average O ₂ content of tank headspace	1.4%	21%
Peroxide value		
Initial	1.0	1.0
Final	1.5	5.0

TABLE 8. Conditions of Plant Storage Test on Refined, Bleached Soybean Oil (38).

The plant-scale samples were placed in storage beginning in mid-summer and thus were exposed to the highest temperatures during the early part of the storage test. The observed peroxide values were 5.0 for the air-stored sample and 1.5 for the nitrogen-stored sample. The study of effects of nitrogen- and air-storage conditions on flavor quality of finished deodorized oils (salad oil and hydrogenated oil) showed a decreased flavor score with storage time at 60 °C (140 °F) for all products. However, the products made with the oil stored in air had a greater rate of flavor score reduction than those from the oil stored under nitrogen. The results clearly demonstrate that even low levels of oxidation products formed while soybean oil is held in bulk storage, although not necessarily harmful to initial quality, have a deleterious effect on shelf life. These results are in accord with Evans et al. (62), who showed that autoxidation of soybean oil prior to deodorization has a detrimental effect on flavor and oxidative stability.

Nitrogen Packaging. A study of the impact of use of nitrogen in consumer packages on soybean oil stability was completed by Evans et al. (61). Eight lots of commercially processed soybean salad oils, representative of those available to American consumers, were obtained for the study. Each lot consisted of 20–40 samples packaged in screw-cap cans and bottles. Headspace gas analysis (63) showed that air, pure nitrogen (0.0% oxygen), and nitrogen containing low levels of oxygen were used to package the samples. All samples were stored in the dark at two temperatures, 25.6 °C and 37.8 °C (78 °F and 100 °F), and flavor evaluation was conducted by a 20-member sensory panel (64).

The effects of nitrogen versus air packaging on the flavor deterioration of hydrogenated-winterized soybean oils (HWSBO) stored in the original containers at 25.6 °C and 37.8 °C (78 °F and 100 °F) for 1 year showed that the initial flavor scores of the nitrogen-protected samples (average 7.5) was similar to the air-packaged samples (average 7.9). However, during 1-year storage, nitrogen-packaged samples only showed loss of approximately one flavor score unit at both 25.6 °C and 37.8 °C (78 °F and 100 °F). By contrast, air-packed samples deteriorated rapidly at both storage temperatures. The effect of storage temperature is pronounced. One sample dropped to a flavor score of 6 in approximately 18 weeks at 25.6 °C (78 °F), whereas equivalent deterioration occurred in less than 6 weeks at 37.8 °C (100 °F). It was found that hydrogenation alone, without added antioxidants, metal scavengers,

and nitrogen packaging, is not sufficient to ensure adequate shelf life of hydrogenated-winterized soybean oil, particularly at elevated storage temperatures.

Oxygen in the headspace of bottled soybean oil greatly affects the storage stability. As the oxygen content of the headspace gas increased, the flavor scores of the oils decreased. A nonhydrogenated oil, protected with antioxidants but with incomplete nitrogen protection (2% oxygen), deteriorated to a flavor score of 5.0 after 18 weeks of storage at 37.8 °C (100 °F). Even so, its stability was greater than that of an air-packaged sample of hydrogenated oil. After several months of storage, loss of flavor score occurred for both hydrogenated and nonhydrogenated samples unless they were protected with nitrogen. The improvement in storage life offered by 100% nitrogen (0% oxygen) over 98% nitrogen (2% oxygen) is obvious. Nitrogen sparging and nitrogen blanketing have been shown to increase the induction phase of the oxidation, and to reduce the rate of accelerated phase of oxidation. The benefits of nitrogen as a protective measure are used widely in the oil industry.

A relatively recent study compared the effects of light, temperature, and nitrogen sparging on the stability of nonhydrogenated and hydrogenated soybean oils in plastic and glass containers (65). Prior research demonstrated that the most effective methods of maintaining the quality of liquid soybean oil was the use of amber glass containers to reduce light exposure and nitrogen packaging to minimize the oxidation of the oil (61). Properties such as oxygen permeability, impact resistance, clarity, and flavor transmission from the bottle material to the food have also been considered by other researchers (66).

Oil samples were packaged in glass and polyvinylchloride (PVC) bottles and sparged with nitrogen for 1 min, then sealed and aged at 25.6 °C (78 °F) for 4, 6, 9, and 12 months. The results of these evaluations indicated no significant difference in the sensory evaluation of the oils aged in the long-term ambient temperature tests regardless of the packaging material used for bottling. In these long-term ambient-temperature studies, HWSBO or SBO show no differences in oil deterioration between glass and PVC packaging. Oils packaged with nitrogen in the head-space treatment in PVC bottles had equivalent flavor stability compared with oils packaged in a similar manner in glass bottles. The conclusion was that PVC bottles were acceptable alternatives to packaging oils in clear glass. The results of this research had a significant impact on the edible oil industry, which, in 1985, converted all consumer soybean oils to translucent plastic bottles.

3.2. Other Deterioration During Extended Storage

Prime concerns in storage of crude and once-refined soybean oils include increases in moisture and volatile matter, color after refining or bleaching, peroxide value, free fatty acids, and refining losses. Aside from possible effects on flavor and oxidative stability, many of these quality factors also affect the commercial value of oil in trading channels. With the exception of peroxide values and refined color, the other quality factors above are written into specifications for oils sold under trading rules of the National Soybean Processors Association (NSPA) (67).

To study the changes in these quality factors, Baumann et al. (59, 60) obtained thirty-six 189.3-L (50-gal) drums of crude, crude-degummed, and once-refined oils. These samples were stored outside (Beltsville, Maryland), exposed to atmospheric conditions, for 4–6 years. The drums were stored under the following conditions to simulate general conditions of storage in large field tanks: painted aluminum, fitted with breathers, and tilted at an angle to permit moisture to drain. Some drums were completely filled to exclude air (designated no-breather drums) and were opened only for sampling. Other drums were half filled (designated half-filled drums).

The study showed that probable changes in the characteristics of once-refined, degummed, and crude oils can be predicted for various periods of storage. Formulas were developed based on statistical interpretations that, in most cases, predicted oil characteristics after storage. In general, moisture and volatile matter contents were not affected by oil type and storage conditions. Color of the refined oils was affected by these treatments. Peroxide values showed that once-refined oils were the least stable to oxidation, followed by crude-degummed, with crude oil being the most stable. Oils stored in no-breather drums had the lowest peroxide values, and oils stored in half-filled drums had the highest peroxide values. Storage of once-refined oils had only a slight effect on free fatty acid content after the 4-year storage period, it increased from 0.058% to 0.135%. As observed with peroxide formation, the increase in free fatty acids is dependent on access to air and to temperature within the storage drum.

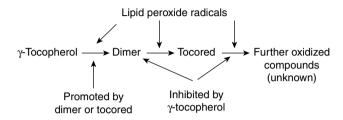
3.3. Color Reversion

Under certain conditions, soybean oil that is refined, bleached, and deodorized to yield a pale light-colored product becomes darker upon storage. This phenomenon, known as color reversion, has been studied in detail by Japanese scientists (68, 69). The degree of color change is dependent on the nature of the raw soybeans, refining and deodorization conditions, storage conditions, temperature, exposure to light, and contact with air during storage. The tendency to undergo color reversion is variable. Some oils require only a few hours to revert, whereas others require several months. In either event, the color becomes paler after it reaches a peak.

The moisture content of the soybeans, going to the extractor, appears to be a key factor in promoting color reversion in fully refined oils. The tocopherol content of extracted oil is markedly affected by the beans' moisture content. Over the normal moisture range (7–12%), the tocopherol content of crude soybean oil remains normal, but in wet beans, the tocopherol content is markedly reduced (68). Subsequent work (69) showed that tocored [2, 7, 8-trimethyl-2 (4', 8', 12' -tridecyl-2)-chromane, 5, 6-quinone] is the precursor of the reversion color, and that this material reaches a maximum in soybeans with moisture contents of 15–18%. This phenomenon was observed by Shukla (unpublished observation) in beans originating from Argentina and was highly related with the moisture content and the ways beans were treated during storage and voyage to Europe.

Other work (70) indicated that no change in the α -tocopherol content of the crude oil was observed by elevating the moisture content of soybeans, but a

decrease in γ - and δ -tocopherols occurred. The decrease in γ - and δ -tocopherols was accompanied by an increase in dimeric oxidation products. The latter effect could be reversed by decreasing the moisture content of the beans. Thus, it appears that color reversion involves oxidation of γ -tocopherol to a dimeric product that, in turn, is converted to tocored. The following mechanism was suggested for color reversion (70):



4. CONCLUSIONS AND FUTURE PERSPECTIVES

This chapter deals with problems involved in treating the vegetable oils at every aspect of production and highlights the sources of errors and how to rectify these with proper management. All attempts should be made to produce the final product with extremely limited destruction, thus keeping the active ingredients and still providing the freshness of the product to be used as ingredient in the food chain. Modern processing technologies provide foods with consistent quality and hygiene. Newer technologies will help to create much cleaner raw materials, thus avoiding the application of complicated processing methods. Thus, foods should be manufactured with simple, greener technologies rather than the complicated chemical technologies as used in the early days (71).

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