Major Factors That Influence Bleaching Performance[1]

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Abstract

The three major factors which affect bleaching performance are type of clay, bleaching method, and oil quality. These are discussed in order.

Under the first are such topics as purpose of clay in industry, source of raw material, clay types, physical structure, effect of activation on structure, variation in effectiveness of clays produced from different raw materials, and mechanism of the clay's action. Also covered is the effect of the clay's properties—moisture, apparent bulk density, specific gravity, acidity, pH, hydrated silica, particle-size distribution, and the theory of variability.

Under the second are effect of bleaching conditions, such as temperature, time, agitation, temperature of clay addition, vacuum *versus* atmospheric bleaching; commercial methods including atmospheric batch, vacuum batch, vacuum continuous; and effect of oil quality.

Under the third are response of different color pigments to bleaching, effect of moisture, oxidation, and organic impurities in the oil.

Of the three factors, oil quality has the greatest influence upon bleaching performance.

Introduction

THE THREE MAJOR FACTORS influencing bleaching performance are clay type, bleaching method, and oil quality. Technical knowledge is fairly well established on the first two, less so on the third. Bleaching has been practiced for more than 50 years and can rightly be termed an "art." However the chemical and physical reactions which underlie its use on oil are highly involved and only partially understood. If they were known, the operation would be much closer to a science.

Effect of Clay Type

The primary purpose of bleaching clay in industry is to reduce the color of the oil, but it also serves to remove other impurities. Both functions are accomplished by adsorption. As an example of removing substances other than color, clay absorbs soap from refined oil. Soap poisons nickel catalyst used in hydrogenation and may cause color reversion during or after deodorization. From the oil clay also adsorbs suspended matter, phosphatides, moisture, and colloidal nickel when bleaching follows hydrogenation.

Bleaching clay is produced from calcium, or nonswelling, bentonite. The latter by definition is clay containing not less than 85% of the mineral montmorillonite, $Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$, on a dry basis (9). The clay's origin is volcanic ash, which is converted to montmorillonite over the years by weathering and hydrothermal chemical reactions. In addition to montmorillonite, clay contains such metallite impurities as iron, calcium, magnesium, sodium, potassium, titanium, etc.

Bleaching clay owes its effectiveness as an adsorbent to the fact that some of the Al ions in the montmorillonite structure have been replaced by hydrogen. Up to a certain point the more Al replaced by H, the greater is the absorptive capacity of the clay or, as expressed in the oil industry, the greater is its bleaching power. This factor accounts for the difference between the two basic types of commercial bleaching clay, natural and activated.

Natural clay is produced from a bentonite that possesses natural bleaching power, *i.e.,* some of the Al has been replaced by H in nature by the leaching action of hydrolyzed pyrites or organic acid waters while the clay was in the deposit. In manufacture it merely is dried and milled.

Activated clay is made from a bentonite that has little natural bleaching power, *i.e.,* the Al ions in the montmorillonite are relatively intact. In manufacture it first is treated with mineral acid ("activated"), which replaces Al with H to a higher degree than on natural clay. The excess acid is removed by washing with water, then the clay is dried and milled.

Natural clay has a lower capacity than activated for adsorbing color and other impurities from oil. But it is nearly neutral whereas activated clay is slightly acidic despite the washing it has received. The advantages of natural clay consequently are less formation of free fatty acid during bleaching and a less deleterious effect upon cotton duck filter cloths. In addition, it is heavier in bulk density than activated clay, which gives it a lower retention of oil.

Adsorption is a surface phenomenon, and most theories advanced, such as those of Freundlich (2), Polyani (5), and orientation, merely measure the extent of adsorption under given conditions. The clay manufacturer knows from experience the effect of replacing Al by H, acidity, moisture, and particle-size distribution in his product, but the reason why clay adsorbs color and other organic impurities from oil remains a mystery.

Moisture. Bleaching clay normally contains from 10–18% free moisture. It is believed that the montmorillonite molecules are arranged in aggregates as parallel layers. The water molecules lie between and around the layers and thus serve as a support to keep the layers apart. If clay is dried prior to bleaching, the layers collapse, resulting in impaired bleacing power because of decreased surface area (9).

However, in bleaching, the color bodies cannot be adsorbed to the clay's maximum capacity until its free moisture has been removed by heating, *i.e.,* the color bodies cannot enter the interstices of the clay to its fullest adsorptive capacity so long as moisture is still there. Sufficient time and temperature must be applied to accomplish this.

Cases have been reported on low-quality fats in which the bleach was enhanced by the addition of water with the clay (7). This probably was caused by coagulation of organic impurities in the fat by the water, which rendered adsorption of color by the clay more effective. There is no evidence that variation within the clay's normal moisture range has any appreciable effect upon the bleach.

Apparent Bulk Density. The apparent bulk density (ABD) of a clay is the wt./unit volume when it has been tapped to constant volume. One of the clay's most informative characteristics and its most important use are to indicate the clay's oil retention (8,9). The ABD depends upon the amount of void space in the clay; the more void space, the lower is the denstiy. Void space occupied by oil in bleaching forms the oil retained in the filter cake. Thus the relationship of ABD to oil retention also is inverse; the lower the ABD, the higher is the retention.

Since activated clay has a lower ABD than natural clay, it has a higher oil retention because of the replacement of Al by lighter H in activation, also the removal of metallic impurities from the clay. Both of these lighten its density.

The acidity of natural clay, if any, is $Fe_2(SO_4)_3$ or $Al_2(SO_4)_3$. The acid salts are formed after hydrolysis of the iron pyrites, an impurity in the clay. In activated clay the predominant acidic substance is the Al salt of the activating acid. Acidity is expressed as titratable acidity or as pH. The former is determined on a water extract of the clay and the latter on a slurry of the clay in water. It might be expected that a consistent inverse relationship exists between the two: the higher the acidity, the lower the pH. While this generally is the case, the relationship

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is irregular because of variability in the buffering effect of the salts on the pH. For example, it is possible for two clays with the same acidity to have widely different pH's and *vice versa.*

Despite the lack of a fixed relationship between the two tests, each is indicative respectively of one phase of bleaching performance. Acidity, but not necessarily pH, is directly related to press-cloth deterioration whereas pH, rather than acidity, is inversely related to the amount of free fatty acid increase in bleaching.

Both a low pH and substantial acidity are indicative of the clay's effectiveness in removing green color from chlorophyll-rich oils, such as soybean, but also the red on other vegetable oils. The reason is that a neutral clay will adsorb green or red color to a certain degree, but the adsorption is enhanced if the clay is slightly acidic.

Hydrated Silica. Hydrated silica is the term used to designate the amount of hydrous silicic acid present in a clay formed as a by-product when Al ions have been replaced by H ions. It is an index of the degree of activation to which the clay has been subjected. Pure montmorillonite contains no hydrated silica; the latter is low in natural clay but relatively high in activated clay. As the hydrated silica increases up to an optimum level, the absorptive capacity of the clay and the oil retention also increase.

Particle-Size Distribution. Particle-size distribution in a clay is the percentage of the different micron size particles present, ranging from the percentage of very fine 0–5 microns to that of coarser than 80 microns. Within limits the more fine particles present, the greater the adsorptive capacity of a clay, but also the higher is its oil retention and the slower it filters.

Effect of Bleaching Method

Bleaching Temperature. Adsorption rate increases with temperature, and the moisture of the clay must be removed for maximum color adsorption; thus in normal bleaching time the temperature should be above the bp of water. But if the temperature is too far above the bp, color darkening may occur by oxidation. Unless a very high vacuum is used, the desired temperature lies in the range 220–230F. Exceptions are bleaching oils that revert in color at temperatures even below the bp, *e.g.,* certain fatty acids in the manufacture of which rigorous oxidative treatment has been employed. In such cases a temperature of 170–180F is used. Palm oil is bleached at temperatures of 300F or higher because it fades readily with heat.

A lighter bleached color is obtained when clay is added to the oil at a temperature below the bp on the "upheat" rather than at the bleaching temperature. Evidently a slow release of the clay's moisture is beneficial because there is a protective blanketing effect against oxidation of the water vapor. When clay is added to hot oil during the upheat, the oil is unprotected in this respect.

Bleaching Time. Theoretically adsorption should be practically instantaneous; however in practice this is not the case. Time is required for the clay to release all its moisture and take up the color pigments to its full capacity; the minimum is 15 minutes at a bleaching temperature above the bp of water.

Even by employing the violent rpm of the AOCS bleach test, which should facilitate contact between clay and color, all moisture is seldom removed from the clay by the end of the 5-min bleach time at 120C, and adsorption is still in progress. In the plant, upheat and filtration times are relatively long, perhaps an hour, during which the clay is in contact with the oil at high temperature, and the degree of adsorption approaches the maximum.

TABLE I

Percent of Cases in which Vacuum or Atmospheric Bleaching Was Superior

	Natural clay		Activated clay	
Oil	Vac.	Atmosp.	Vac.	Atmosp.
Soybean	0	100	94	6
Cottonseed	0	100	93	7
Linseed	....	....	71	29
Inedible tallow	0	100	8	92

Agitation. Agitation should be sufficient vigorous to achieve intimate contact as quickly as possible between clay and color pigments. Violence is needless and promotes oxidation if air is present.

Vacuum vs. Atmospheric Bleaching. Table I summarizes the percent of cases in the Bennett-Clark laboratory in which vacuum or atmospheric bleaching showed decolorizing superiority when the two methods were conducted under the same conditions of temperature and time. Included are both natural and activated clay on a number of oils. Atmospheric bleaching with natural clay was superior in all cases regardless of the oil. Atmospheric bleaching with activated clay was superior on tallow, but vacuum bleaching was preponderantly superior on all three vegetable oils.

The reason for these variations is attributed to oxidation, which may lighten (fade) or darken (form) color in oil during bleaching, depending upon the nature of the color pigments present and the oxidative state of the oil (4,9). Clay acts catalytically to promote one effect or the other in addition to adsorbing color. Under vacuum the two oxidative side-effects are minimized, and color adsorption should be the sole effect. In the atmosphere all three effects may occur. Natural clay, being practically neutral, is a weak oxidation catalyst and promotes little color formation in the atmospheric bleach but apparently some fading. Thus its atmospheric bleach was superior on all the oils.

Activated clay is slightly acidic and possesses high surface area, consequently it is a relatively strong oxidation catalyst. It evidently formed more color than it faded on the vegetable oils in the atmosphere, therefore the atmospheric bleach was inferior. On tallow in the atmosphere, fading predominated over color formation because of considerable carotene in the fat, which readily fades with oxidation.

The three common types of commercial bleaching methods used on fats and oils are batch atmospheric, batch vacuum, and continuous vacuum. This sequence also is the chronological order in which they were developed in the industry.

Batch Atmospheric. Oil at approximately 160F is pumped into an open tank provided with steam coils, or steam jacket, and a paddle agitator. Clay is added from the top of the tank with agitator running; the temperature is raised to bleaching level, at which it is maintained for a short time. The clay-oil slurry next is recirculated through a filter press and back to the bleach tank until the oil is clear, then the oil is pumped to storage.

Batch Vacuum. Clay is added to an open slurry tank containing a portion of the oil to be bleached at approximately 160F, then it is pumped to the vacuum bleach tank containing the balance of oil. The latter is under approximately 27–28 in. of vacuum and, like the open bleach tank, is equipped with coils or steam jacket and agitator. After the prescribed time at bleaching temperature, the slurry is cooled to approximately 160F, the vacuum is broken, and the slurry is filtered.

Continuous Vacuum. Continuous vacuum bleaching is the newest of the three systems. Clay is fed continuously from an automatic feeder hopper to the oil at a temperature of 160F. The rate of clay addition can be regulated to whatever dosage is desired. In one unit the slurry is heated to bleaching temperature (approximately 210F) and conveyed continuously in and out of a vacuum bleach tank, which is equipped with a Turbo agitator and level control to provide a given detention time. It then is cooled, the vacuum is broken, and the slurry is filtered.

Another system sprays the slurry continuously into a vacuum aeration chamber at 160F to remove both water and air from clay and oil. The temperature is raised to bleaching level in a heat exchanger, and the slurry is fed continuously into a second chamber for bleaching. It then

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Bleaching Performance . . .

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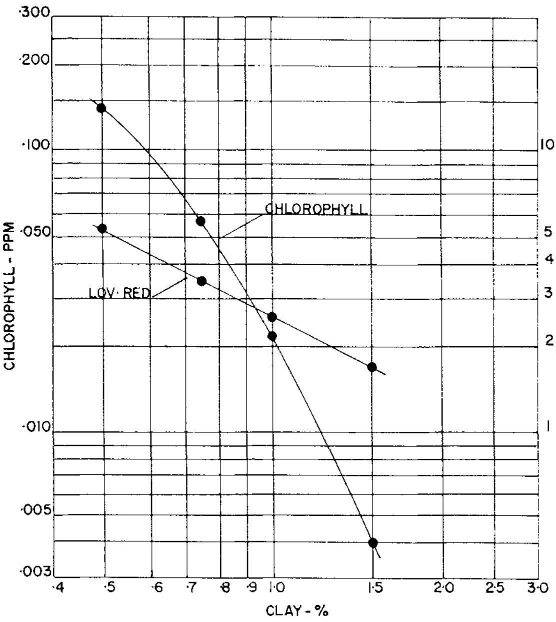

FIG. 1. Chlorophyll and Lovibond red *vs.* % activated clay-refined soybean oil.

is filtered in a closed-type press and cooled; the vacuum is broken.

Batch bleaching is preferable to continuous when a variety of oils is handled, each of which is of relatively small volume. But if only a few oils are treated, continuous bleaching is better because large volumes can be processed without frequent shutting down to refill the bleach tank. Also the bleached color can be regulated as the operation progresses. Since the system is almost automatic, the operators can employ part of their time elsewhere.

Both batch and continuous vacuum possess a number of advantages over batch atmospheric bleaching. Under vacuum, color can be obtained on vegetable oil with less activated clay. Also the bleached oil's keeping quality is superior because of minimized exposure to oxidation, FFA increase is lower because moisture is removed more rapidly and hydrolysis is reduced, the operation is cleaner. Most vegetable oil bleach plants built domestically in recent years have been vacuum, and a number of them are continuous.

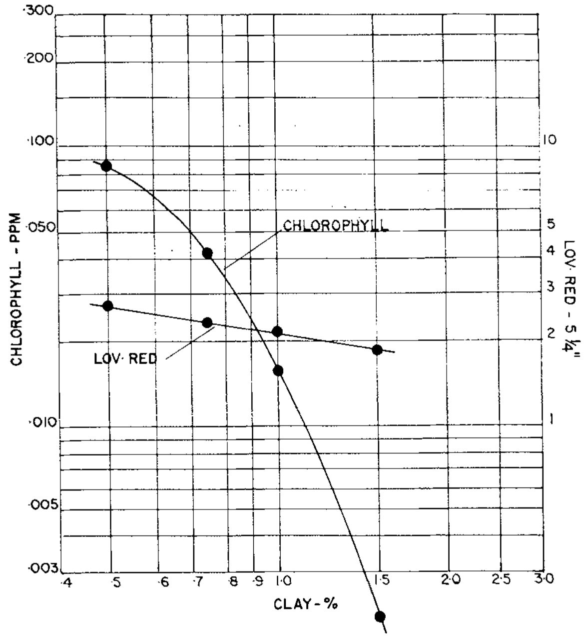

FIG. 2. Chlorophyll and Lovibond red *vs.* % activated clay-refined cottonseed oil.

TABLE II

Enhanced Reduction of Lovibond Red and Chlorophyll by Clay Acidity on Refined Soybean Oil

Clay	Clay %	Lovibond Red 5¼ in.	Chlorophyll ppm
(Refined oil)	....	10.0	.800
Neutral natural clay	1.2	4.7	.123
Same acidified	1.2	3.1	.071

Effect of Oil Quality

Oil quality more than any other factor governs bleaching performance. Differences between clays on a given oil, or between bleach methods, are of minor magnitude compared with those of bleaching two oils of different quality when the same clay and bleaching method are used. A clay activated to the highest adsorptive capacity possible, using the most effective bleaching conditions, gives poor results on an under-refined or oxidized oil. Among the oil quality categories the one most vital to bleaching performance is organic impurities (O.I.) in the oil; next is the oil's oxidative state.

Response of Different Color Pigments to Bleaching. The green color in soybean and cottonseed oils is chiefly chlorophyll, either chlorophyll A ($C_{55}N_{72}MgN_4O_5$), chlorophyll B ($C_{55}H_{70}MgN_4O_6$), or both. The red-yellow color consists of *alpha* or *beta* carotene (both $C_{40}H_{56}$) and xanthophyll ($C_{40}H_{56}O_2$). Cottonseed oil also contains the gossypol pigments. All these pigments are complex organic compounds, containing a number of double bonds, so they can be attacked by oxygen. Hereafter green color will be designated as "chlorophyll."

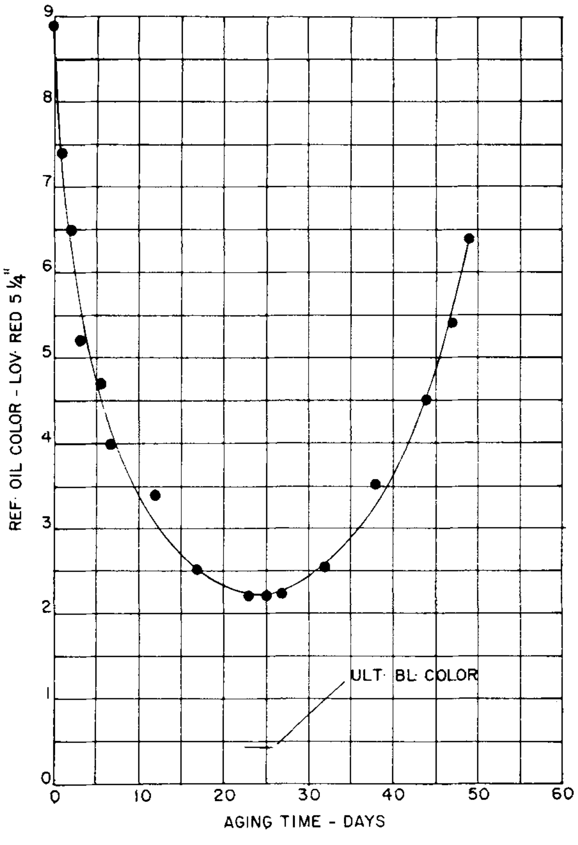

FIG. 3. Effect of aging refined soybean oil at 240F on its color.