

TABLE VI  
Effect of Active Content on Cakiness

	Breaking force required, lb		
	20% Active	25% Active	30% Active
Drum-dried light duty product.....	31.0	37.9	39.8

products from studies on their drum-dried counterparts. It is even more difficult to predict how a product will respond in a heavy duty spray-dried form from studies on light duty drum-dried samples.

*Anticaking Agent.* It is well known that the addition of certain compounds to dried detergents decreases the caking tendency. Among the more common of these anticaking agents are xylene and toluene sulfonate. This test showed that light duty drum-dried detergents containing 5% xylene or toluene sulfonate have a significantly lower caking tendency. This shows in Table V.

*Formulation Effects.* The results shown in Table VI indicate the caking tendency of a product varies directly with the active content. This work was done with a drum-dried, light duty formulation.

In addition to changes in cakiness as a results of variation in active content are those brought about by builder changes, i.e., by going to heavy duty

TABLE VII  
Light Duty vs. Heavy Duty Formulation

Product	Breaking force, lb	
	HD	LD
Commercial spray dried.....	7	15
Lab-drum dried.....	20.5	35.3

formulations. The basic difference is, of course, the replacement of much of the sodium sulfate with polyphosphates. The cakiness of a heavy duty product is generally less than that of a comparable light duty. This does not necessarily mean that any heavy duty has a lower caking tendency than any light duty. The results show in Table VII were obtained using products containing about 30% active sulfonate, and the balance being sodium sulfate and chloride in the light duty with ca. two-thirds of the sulfate replaced with polyphosphate in the heavy duty.

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[Received October 21, 1963—Accepted January 7, 1963]

## Some Basic Factors in the Bleaching of Fatty Oils<sup>1</sup>

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### Abstract

The physical and chemical properties of bleaching clay are presented, and the effects of these properties upon its performance in bleaching. Various bleaching effects are described:

- 1) Comparison of atmospheric vs. vacuum bleaching, showing the superiority of one or the other depends upon the predominance of oxidative color fading or color fixation/color formation in the atmospheric bleach.
- 2) The log-log bleach curve of clays carried out to extreme dosage.
- 3) Bleaching time-temp effects on different oils, showing that up to a given time, high temp bleaching gives a lighter color than low temp; however, with increased time the high temp bleached oil darkens rapidly in contrast to the low temp oil, which levels out with time.
- 4) The effect of adding clay to hot oil vs. adding it to "cold" oil, indicating a better bleach when the clay is added to the cold oil, with an explanation for the effect.
- 5) Comparison of bleaching by filtration of the oil through a layer of clay against conventional bleaching, indicating superiority for the former.

### Introduction

VEGETABLE OIL bleaching is a highly controversial subject. Mechanically it is a simple operation: clay is added to oil, followed by increasing the temp

to a given level with the oil under agitation, maintaining the temp at that level for a given time, then separating the clay from the oil by filtration. However, the chemical and physical principles underlying bleaching are highly complex and only vaguely understood. In fact the resulting effects on oil color often are so contradictory that bleaching has been termed an "art of witchcraft."

In this presentation an attempt will be made to clarify some of the basic facts about bleaching—specifically: first, to outline the nature of bleaching clay and the theories connected with its use; secondly, to discuss the effects of some of the clay's properties on its performance in bleaching; and last, to describe a number of observed effects in bleaching that appear to follow a consistent pattern.

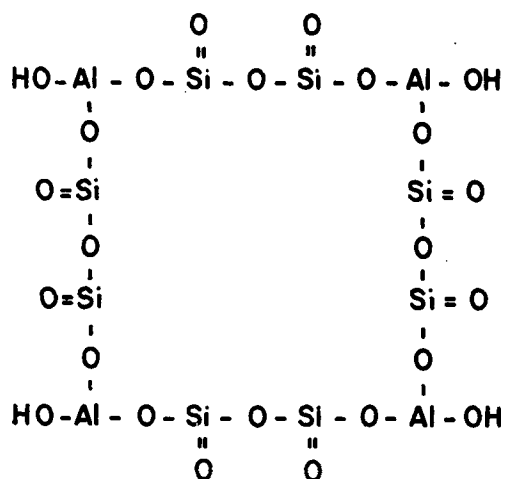
### Nature of Bleaching Clay and Theories of Adsorption

Bleaching clay is produced from a calcium bentonite, which is loosely defined as a clay containing not less than 85% of the mineral montmorillonite (1) on a dry basis. As is well known, there are two types of bleaching clay—natural and activated.

Natural clay is made from bentonite possessing a natural ability to bleach oil, or more correctly, to remove color bodies from oil by the process of adsorption. This bleaching clay is merely dried and milled to a powder with a given particle size distribution.

Activated clay also is produced from calcium bentonite, but it usually is a bentonite that has little ability in the natural state to remove color from oil. In its manufacture the clay is treated with mineral acid, followed by removal of excess acid, before drying and milling.

<sup>1</sup> Presented at the AOCs Northeast Section Meeting, April, 1963.



(PLUS 3HOH WATER OF CRYSTALLIZATION)  
= 6.98%

Fig. 1. Empirical formula of montmorillonite.

Figure 1 presents the chemical formula for montmorillonite—the key substance in bleaching clay. For simplicity it is represented in the form of a square with an aluminum ion at each corner. The formula also includes some water of crystallization, which appears to average three moles. The water of crystallization does not enter into either activation of the clay or bleaching, as it is stable to temp up to 400–500F, so may be ignored for all practical purposes. Calcium, magnesium, iron, and other metallic ions in the clay are present as impurities, and are not included in the montmorillonite formula.

In natural clay some of the aluminum ions in the montmorillonite have been replaced by hydrogen ions from the leaching action of hydrolyzed pyrites or organic acid waters over long periods of time while the clay was in the ground. Thus natural clay has been mildly activated by nature. The acquisition of the hydrogen ions in place of the aluminum ions is one of the factors that gives clay its ability to adsorb color pigments from oil.

In the case of activated clay, the treatment of the bentonite with mineral acid exchanges hydrogen ions from the acid for aluminum ions artificially, and the replacement can be controlled to whatever degree of activation is desired. Activated clay has more aluminum ions replaced and higher surface area than has natural clay, and thereby possesses a greater adsorptive capacity.

The effects of some of the properties of bleaching clay upon its performance in bleaching vegetable oil will be discussed below.

There are three major types of color in vegetable oil:

1. Organic color pigments of known composition.
2. Organic degradation products.
3. Color formed by oxidation of colorless precursors.

In the unoxidized state, the principal organic color pigments of known composition are quite readily adsorbed by bleaching clays. Pigments in the most common vegetable oils are:

*Alpha, Beta Carotene* ( $C_{40}H_{56}$ ). The carotenes are yellow to red, and structurally consist of highly unsaturated hydrocarbon chains arranged in various

cyclic configurations. An important characteristic of the carotenoid pigments from the standpoint of bleaching is that they are unstable to heat and, as oxidation progresses, they gradually fade practically to a colorless state.

*Xanthophyll* ( $C_{40}H_{56}O_2$ ). Xanthophyll is colored yellow, and it is structurally similar to the carotenes except for an extra oxygen in the cyclic ring at each end of the hydrocarbon chain.

*Chlorophyll A and B* ( $C_{55}H_{72}MgN_4O_5$ ) and ( $C_{55}H_{70}MgN_4O_6$ ). The chlorophylls are green, and structurally are unsaturated magnesium—containing pyrrol derivatives and esters of the unsaturated primary alcohol phytol. Unlike the carotenoid pigments, the chlorophylls do not fade appreciably on heating. They are more readily adsorbed by clay with low pH (2) because alkali tends to stabilize chlorophyll, whereas acid decomposes it.

*Gossypol Pigments*. The gossypols are the complex system of red, yellow, etc. pigments in cottonseed oil.

The organic degradation products are brown in color, and are present in vegetable oil, usually from damaged seeds. They generally are composed of degraded proteins, carbohydrates, mucilaginous matter, and phospholipids, and normally are present as positive colloid dispersions rather than being oil soluble as are the organic color pigments mentioned above. This type of color is usually difficult to remove by adsorption.

Color formed in oil by oxidation of colorless precursors, such as dark red chroman-5, 6-quinones (3) from gamma tocopherol, is difficult to remove by adsorption. It has been known for some years that as a vegetable oil or animal fat ages, it becomes progressively more difficult to bleach; i.e., more clay is required to bleach oil to the same color. If the aged oil is darker than it was when fresh, the decrease in bleaching response is probably due to the formation of new color which is difficult to adsorb. On the other hand, if the oil is lighter in color upon aging, the color pigments have become fixed, or non-responsive to adsorption, in all probability by oxidation.

Thus it is evident that bleaching is a complex mechanism, and involves more than simple adsorption of color pigments. Some of the color bodies, such as the carotenoids, tend to fade out in bleaching if oxidized by heating. Other new color may form, also by oxidation, and some of the existing color pigments may become fixed (or non-responsive to adsorption) by oxidation which gives the same effect as a poorer bleach.

The mechanism of oil bleaching was well expressed by King and Wharton (4) when they stated that bleaching has two factors working in its favor (i.e., *lowering* color)—adsorption and color fading by oxidation, and two factors working against it (i.e., to *darken* color)—new color formation and color fixation, both by oxidation. The effects of these factors will be discussed later on when comparing atmospheric and vacuum bleaching.

The published theories underlying the adsorption of color from oil differ in the explanation of the phenomenon, including a difference as to whether adsorption is physical, chemical, or both. When a vegetable oil is bleached in the laboratory, then filtered through a Buchner funnel, the coloring matter can be readily removed from the cake at room temp by extraction with a solvent consisting of acetone, isopropyl alcohol, and benzene. Also, the extracted

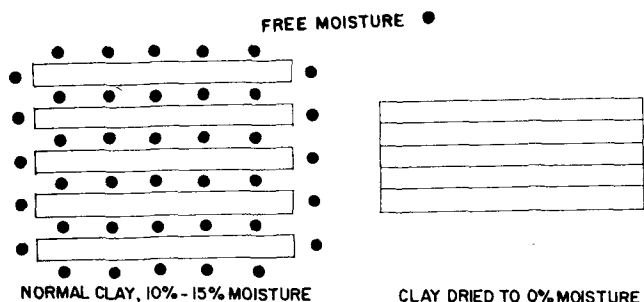


Fig. 2. Schematic diagram of moisture in the montmorillonite lattice.

clay can be used again to bleach more oil with virtually the same adsorptive capacity it had originally. This indicates that the once-used clay was unimpaired during the initial bleach. It may be concluded, then, that the bond of attraction between adsorbent and color body is relatively weak—hence the mechanism of adsorption is probably physical.

Adsorption is a surface phenomenon, and most theories advanced, such as the Freundlich (5), Polanyi (6) and Orientation theories, measure the extent of adsorption under given conditions with a fair degree of accuracy. However, the true explanation of why a clay adsorbs color bodies remains a mystery, and this discussion will be confined henceforth to observed effects in bleaching rather than with theories.

**Effects of a Clay's Properties on Its Performance in Bleaching**

**Moisture**

Figure 2 illustrates the position of free moisture in the clay lattice structure. Bleaching clays normally contain from 10–18% free moisture. The most generally accepted conception of the clay structure is that the montmorillonite molecules are arranged in aggregates in the form of parallel layers, somewhat like a cake. The water molecules lie between and around the layers, and serve as a support to keep the layers apart.

When a clay is dried, the water molecules escape, and the layers collapse. This reduces the active surface area, thereby reducing the adsorptive capacity of the clay. The effect can be easily demonstrated by conducting bleach tests on the clay before and after complete drying, respectively. In every case the dried clay will give a poorer bleach despite the fact that more 100% dry clay is present/g of adsorbent.

However, when bleaching oil it is necessary to remove the moisture from the clay to obtain optimum adsorptive capacity. The color bodies cannot be adsorbed to the maximum capacity of the clay until all the water has been removed, or to express it simply, the color bodies cannot come in until the water goes out. To achieve maximum adsorption, the clay must be added at an oil temp below the bp of water at the pressure employed in bleaching, and the temp of the oil gradually increased to a point somewhat above the bp.

**Clay Acidity**

Natural clay has a normal pH range of 4.0–7.0, and activated clay 2.5–4.0.

As mentioned earlier, chlorophyll-rich oils such as soybean, require a low pH, i.e. substantial acidity, for optimum adsorptive capacity. It is one reason why

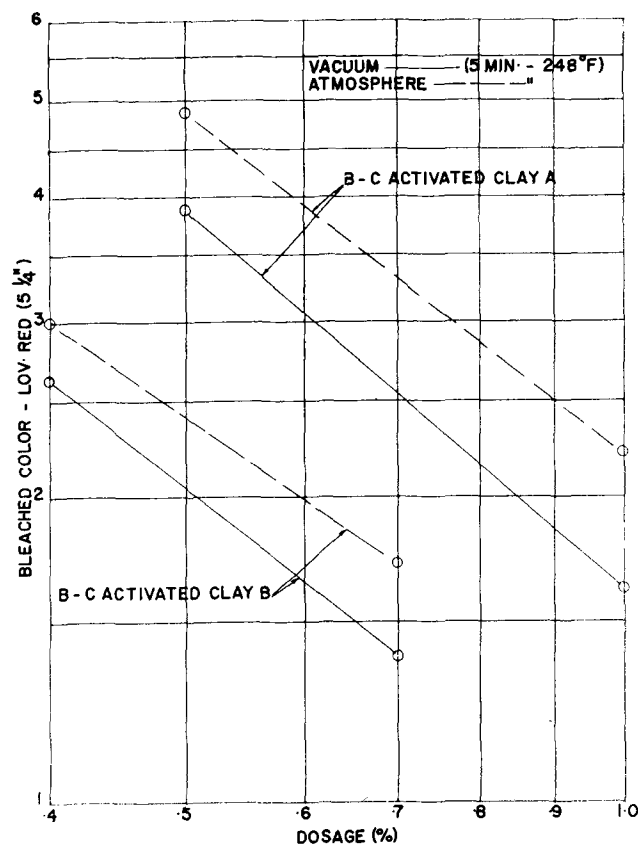


Fig. 3. Atmospheric vs. vacuum bleaching of soybean oil.

natural clay, with its high pH and near neutrality, is relatively ineffective on this type of oil. On other vegetable oils, either lower in chlorophyll or completely deficient, the clay's pH evidently is not as critical.

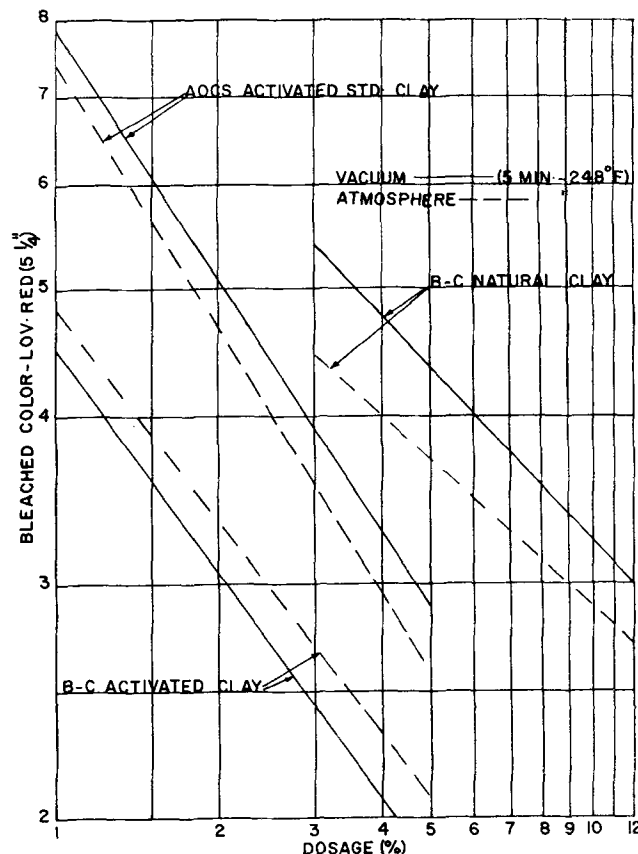


Fig. 4. Atmospheric vs. vacuum bleaching of cottonseed oil.

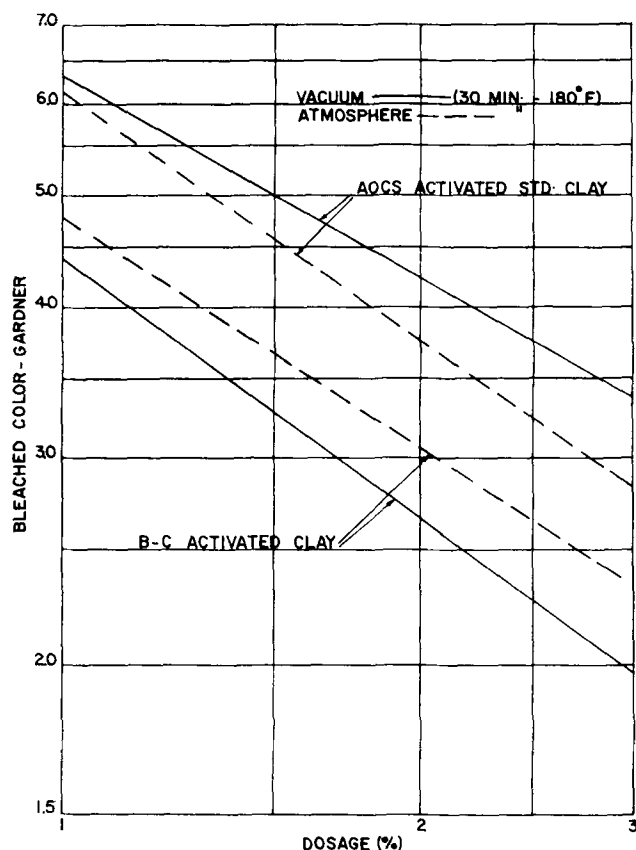


FIG. 5. Atmospheric vs. vacuum bleaching of linseed oil.

While a low pH with substantial acidity is desirable in the clay for bleaching the chlorophyll-type oil, low pH also has a detrimental effect. There is an inverse ratio between clay pH and free fatty acid increase in the oil during bleaching. The hydrogen ions cause some hydrolysis of the oil glycerides to form free fatty acid and glycerine.

For this reason an optimum balance must be observed by the clay manufacturer between a low pH for maximum adsorptive capacity on the chlorophyll-type oils, and a high pH for minimum hydrolytic effect on any fat or oil.

As a matter of interest, the acidity of a clay consists predominantly of the acidic aluminum salt of the activating acid, the balance being free acid. This means that pH buffering, or raising the pH from the theoretical, is caused by the acidic salt when the pH is determined in the usual manner in water medium. Also the clay itself buffers the pH.

#### Apparent Bulk Density

Apparent bulk density (ABD) means the wt/unit vol of clay when it has been tapped to constant vol in a graduated cylinder. It usually is expressed as lb/cubic foot.

The ABD of a clay is one of its most informative properties. For example, the ABD is inversely proportional to the adsorptive capacity and to the clay's filtration rate expressed in sec, or some time unit. Its most significant correlative value is as a measure of the clay's oil retention (7) because the ABD depends upon the air void space in the clay, which in turn measures directly the amount of oil the clay will retain as a filter cake. It can be readily seen that the lighter the clay the more oil it will soak up; thus the ABD is inversely proportional to oil retention.

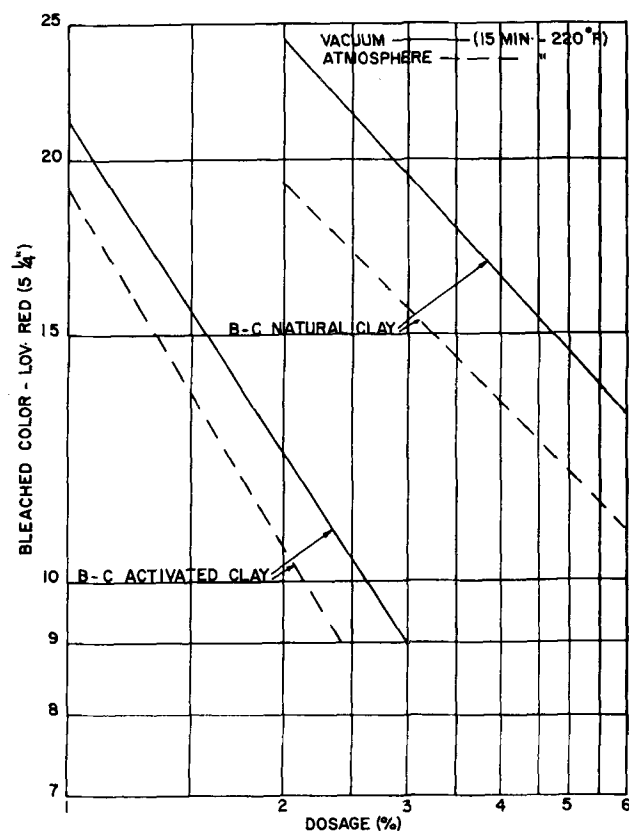


FIG. 6. Atmospheric vs. vacuum bleaching of prime tallow.

There are other clay characteristics which have a bearing on its performance in bleaching, but they are not discussed here because of space limitations. Among these are the particle size distribution, which affects the clay's adsorptive capacity, oil retention, and filter rate, also one of the most vital characteristics of all—hydrated silica, which is a measure of activation.

#### Miscellaneous Bleaching Effects

*Atmospheric vs. Vacuum Bleaching.* Mention has been made that bleaching with clay, besides adsorption, also involves other reactions of oxidative nature occurring during the bleaching period. These oxidative reactions result in a balance between the fading of some color pigments which lightens the color, and the formation of new nonadsorbable color plus the fixation of others which darken the bleached color. The effect of the oxidative reactions is most strikingly demonstrated when comparing atmospheric to vacuum bleaching.

Figures 3-6 illustrate atmospheric vs. vacuum bleaching on three vegetable oils and a tallow, respectively. In these tests, the two types of bleaching—atmospheric and vacuum—where conducted under the same conditions of temp and contact time. It will be noted that in some instances the atmospheric bleach was better, in others the vacuum bleach.

*When atmospheric bleaching is superior,* the fading of color in the atmospheric bleach exceeds new color formation plus fixation of existing color, whereas in the vacuum bleach these oxidative effects are negligible due to the absence of oxygen.

*When vacuum bleaching is superior,* fading of color is exceeded by new color formation plus color fixation in the atmospheric bleach, again assuming that these oxidative effects are negligible under vacuum.

It will be noted that natural clay bleached better in the atmosphere, whereas activated clay, in a majority of cases, bleached better under vacuum.

Natural clay is an oxidation catalyst of low activity because of its low surface area and high pH, consequently in the atmospheric bleach it was not responsible for forming new color or fixing color to the extent color was faded. As a result, the atmospheric bleach was superior to the vacuum in which, theoretically at least, these oxidative effects do not occur.

The results on activated clay were mixed. In four of seven cases, vacuum bleaching was superior, indicating more pronounced color formation or color fixation in the atmosphere. Of the three cases in which atmospheric bleaching was better, two were made with AOCS Official Activated Clay—a clay of low adsorptive capacity, and hence a weak oxidation catalyst.

The third case was on a tallow which had a strong tendency to fade merely exposed to light, so that when it was bleached in the atmosphere with a clay of high adsorptive capacity, fading exceeded color formation or fixation. This demonstrates that the nature and oxidative state of the oil or fat also is a factor in determining whether atmospheric or vacuum bleaching is superior purely from the standpoint of color removal.

Figure 7 is a hypothetical illustration of possible color fading, and color forming (or color fixing) effects based upon actual vacuum and atmospheric bleaches obtained with activated clay and natural clay, respectively, on refined cottonseed oil.

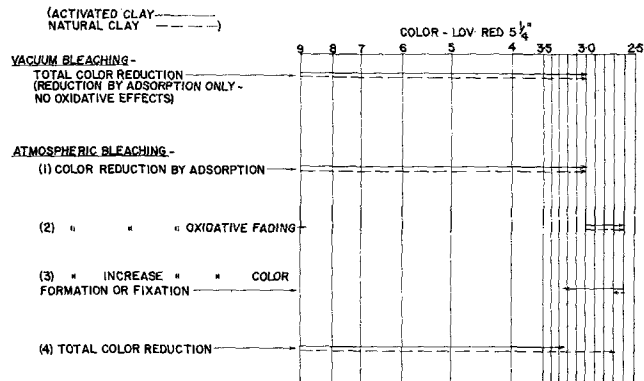


FIG. 7. Hypothetical illustration of plus and minus effects upon color occurring in vacuum and atmospheric bleaching.

The bleached color under vacuum was 3.0 red, and in the atmosphere 3.25 red, using the same percentage of activated clay. Since theoretically there are no oxidative reactions under vacuum, it may be assumed the reduction of color to 3.0 red was due entirely to adsorption. In the atmosphere, it may be assumed the color reduction due to adsorption alone was the same as under vacuum—to 3.0 red. Let's assume color fading by oxidation lowered it another 0.4 red to 2.6 red, then color formation or color fixation darkened the color by 0.65 red, giving the 3.25 red atmospheric bleach obtained.

Enough natural clay then was used to give a vacuum bleach of 3.0 red, all by adsorption. The atmospheric bleach with this percentage of natural clay was 2.7 red. Assuming color fading was 0.4

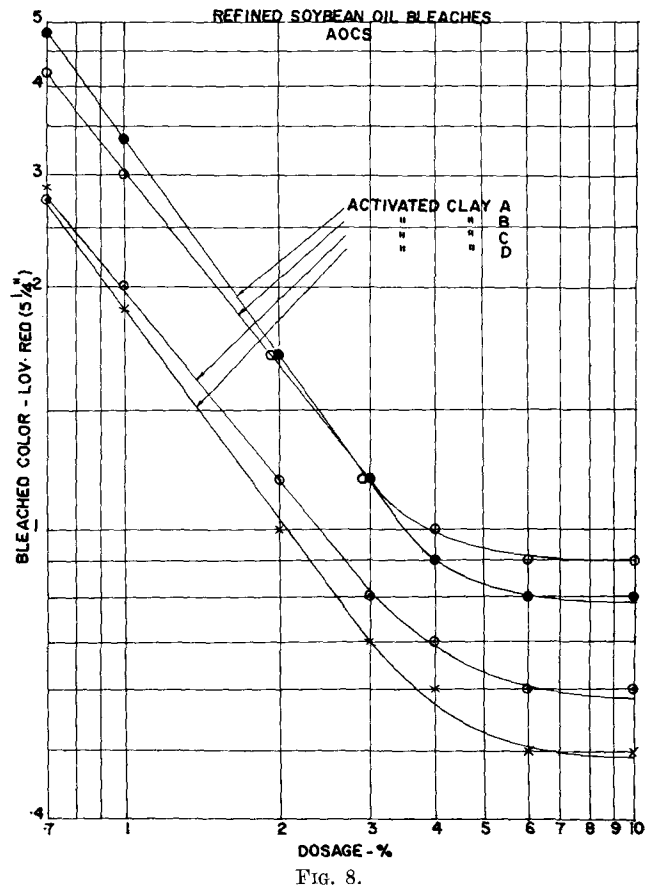


FIG. 8.

red, the same as with activated clay, color formation or color fixation darkened the oil by only 0.1 red to give the 2.7 bleached color obtained. The low degree of darkening was due to the weaker catalytic oxidative effect of the natural clay compared to that of the activated clay.

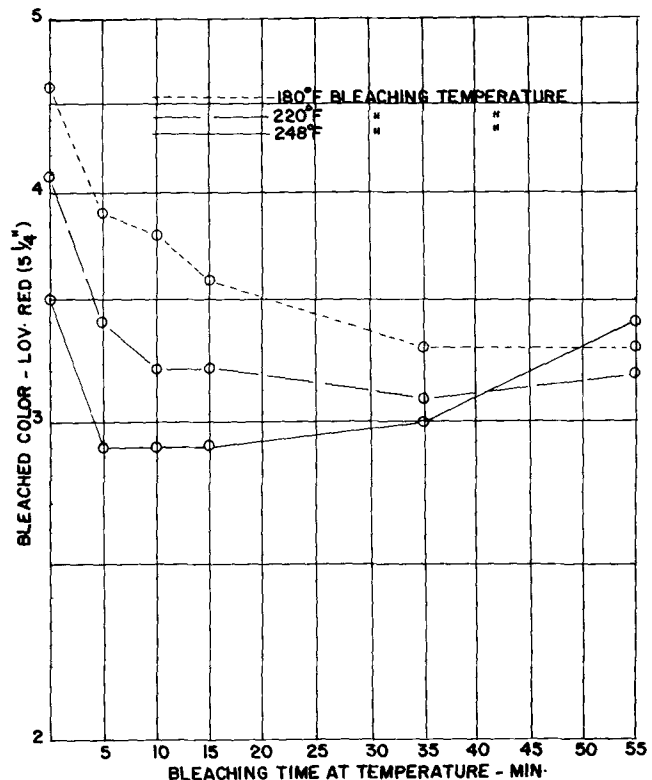


FIG. 9. Time-temp effects upon color of refined soybean oil, using 0.75% activated clay.

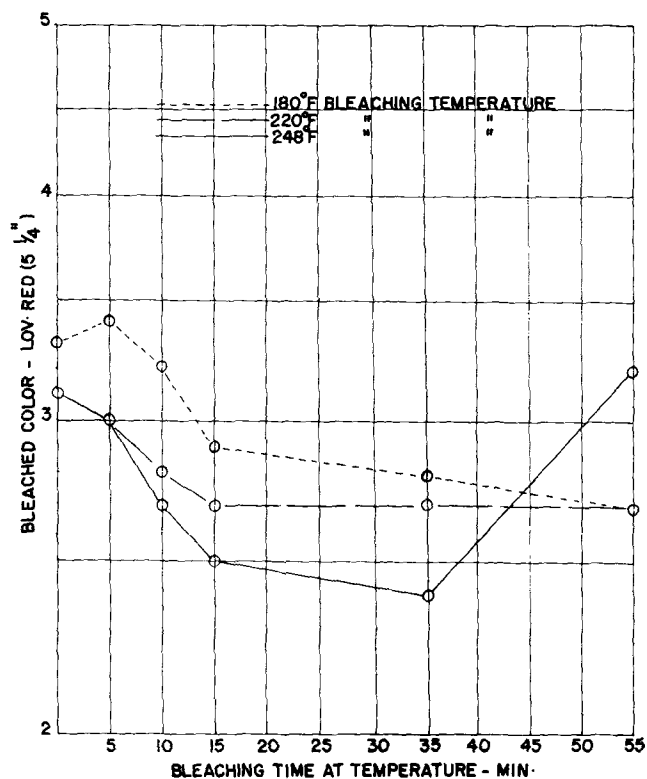


FIG. 10. Time-temp effects upon color of refined cottonseed oil, using 2% activated clay.

It may be concluded that the bleached color superiority of atmospheric or vacuum bleaching, based dominance of color fading or new color formation purely on color reduction, depends upon the pre-plus color fixation in the atmospheric bleach. This is governed to some extent by the strength of the adsorbent as an oxidation catalyst, but also by the tendency of the oil itself to fade or become fixed in color or develop new color on heating alone. As mentioned, activated clay in the majority of cases bleached better under vacuum because it is a relatively strong oxidation catalyst, whereas natural clay bleached better in the atmosphere because it is only a mild oxidation catalyst.

*Bleach Curve of Clays Carried Out to Extreme Dosage.* Figure 8 illustrates what happens to the bleach curve when the clay dosage applied is as high as 10%. These bleaches were made in the atmosphere on refined soybean oil using four activated clays, and it will be noted that the curves on a log-log scale began to flatten out at ca. 3% clay dosage. Clays A and B crossed at about 1.3 red, and remained crossed with increasing dosage.

*Bleaching Time-Temperature Effects.* Time and temp play an important part in bleaching. Figures 9,10 show the effect both of time and temp upon the bleached color of refined soybean oil and refined cottonseed oil, respectively. At 180F the color lightened gradually with time and then levelled off. At 220F, the color decreased to a lower level than at 180F, then levelled off. At 248F, the color decreased to the lowest level of the three temp but after a time began to darken, and after 55 min was darker than after 5 min at either of the other temp. This was due to new color formation which the clay was unable to adsorb.

The optimum bleaching temp on these two oils, using the clays employed, might be considered to be

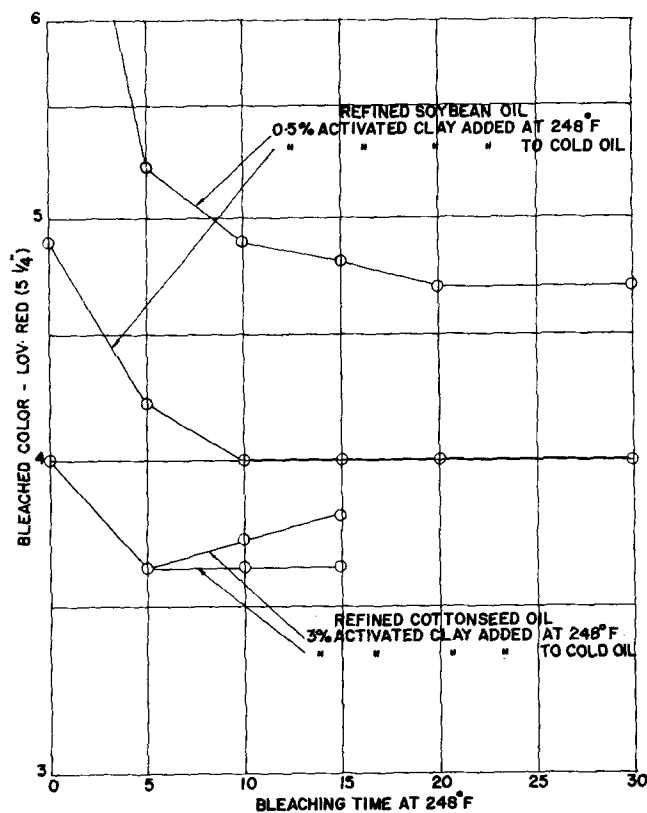


FIG. 11. Addition of clay to cold oil vs. oil at 248F.

248F; however the temp would have to be qualified by a time limitation. It also would have to be qualified by the type and size of the bleaching equipment, and by the specific clay used.

*Effect of Adding Clay to Hot Oil vs. Adding it to "Cold" Oil.* Figure 11 shows what occurred when clay was added to refined soybean and cottonseed oils at 248F, compared to adding it to the oil at room temp, with increasing time of contact. Figure 12 illustrates the same effect upon Fancy Tallow. In all three cases the final bleached color was darker when the clay was added to the hot oil, and the smallest differential occurred on the off-quality cottonseed oil.

The effect evidently is due to one, or both, of two factors:

- 1) Adding clay to hot oil reduces its adsorptive capacity because the moisture of the clay is driven off rapidly, causing collapse of the clay's lattice structure, which in turn lowers its surface area before the clay has had an opportunity to adsorb color.
- 2) Adding clay to hot oil means that during the upheal the oil is unprotected against oxidation, and hence some color fixation occurs. On the other hand, when the oil is heated in the presence of clay, the slow release of moisture from the clay "blankets," the oil with moisture vapor, affording some protection against oxidative color fixation.

The following test illustrates the protective effect of the moisture in the clay. Refined soybean oil was bleached by the official AOCs method in which activated clay was added to the "cold" oil. Some of the same oil was heated first to 248F without clay, cooled, and then bleached with the same clay, again

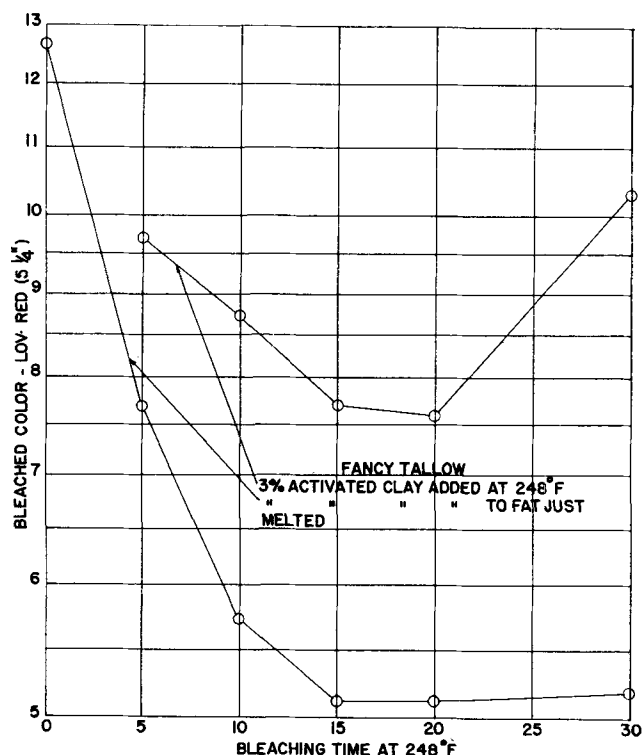


FIG. 12. Addition of clay to cold fat vs. to fat at 248F.

using the official AOCS method:

	1/2% Clay	1% Clay
Bleached color on the unheated oil (Lov. Red)	5.0	2.35
Bleached color on the heated then cooled (Lov. Red)	5.3	2.6

**Bleaching by Filtration of the Oil Through a Clay Layer vs. Conventional Bleaching**

It has been common knowledge for some time that the clay's total adsorptive capacity is never used up in bleaching. "Spent" cake invariably possesses a substantial bleaching power. It also is known that the plant's bleached color usually is lighter than the laboratory bleached color, using the same percentage of clay on the same oil at the same bleaching temp. The plant superiority is generally attributed to these factors:

- 1) Less oxidative effects due to the greater volume of oil and less violent agitation.
- 2) More complete removal of moisture from the clay because of the longer time of contact in the plant.
- 3) Filtration of the oil in the plant through a gradually increasing layer of clay filter cake which, as stated, still retains considerable adsorptive capacity.

An interesting utilization of the plant's filter cake advantage is to compare the color of oil filtered at bleaching temp through a previously prepared layer of clay cake against the conventional bleached color using the same clay. In Figure 13 an activated clay of high adsorptive capacity and low moisture was used for this comparison in order to provide maximum speed of adsorption. The conventional atmospheric bleach curve was obtained on the clay, also on the AOCS Official Activated Clay, to illustrate the high adsorptive capacity of the former.

A slurry was made consisting of the full 0.7% dos-

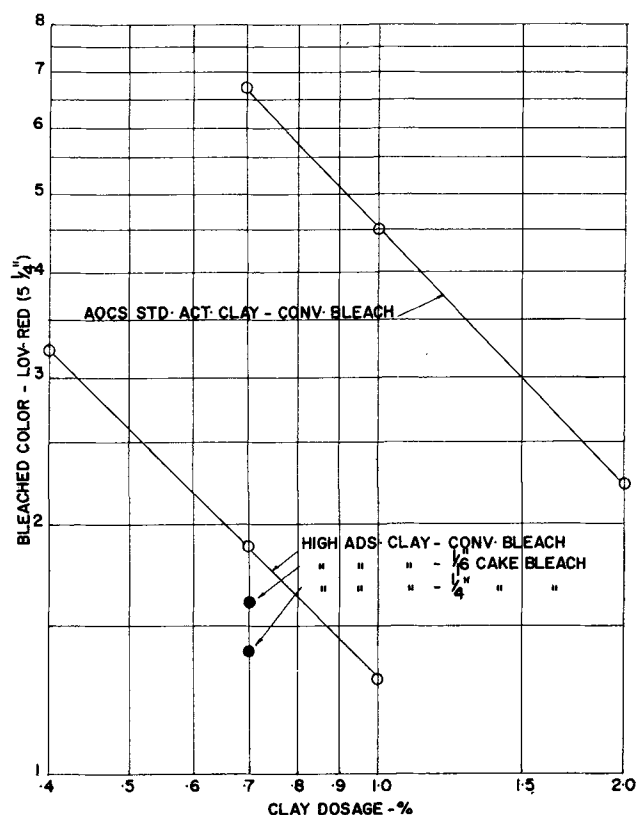


FIG. 13. Bleaching through a clay cake vs. conventional bleaching—refined soybean oil.

age of the high adsorptive clay with 10% of the oil to be bleached, which then was filtered through a Buchner funnel of a diameter that gave a 1/16 in. clay cake. The 90% balance of the oil to be bleached next was filtered through the cake at 248F bleaching temp, same as was used in the conventional bleach. Bleached color of a composite of the oil filtered was 1.6 red vs. 1.9 red for the conventional bleach using 0.7% clay.

When the cake was increased to 1/4 in., again using 0.7% clay with the same temp oil, the bleached color was 1.4 red. It was noted that the bleached color of the oil gradually darkened with time during filtration; however, the overall bleach on the filtered oil was lighter in color than that in the conventional bleach.

Evidently the adsorption of color under these conditions is practically instantaneous, in particular with the low moisture in the clay. Also there is insufficient time for detrimental oxidative color development, or color fixation, to occur. The high adsorptive effect in such a short time of contact (a sec or two) may have been the result of a relatively small amount of oil being in contact with a very large amount of adsorbent during that short interval, or in other words, a mass effect occurred.

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[Received May 21, 1963—Accepted December 26, 1963]