

Oxidation Effects in Adsorption Bleaching of Vegetable Oils¹

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ABSTRACT

In bleaching fatty oils an equilibrium exists between two reactions favorable and two unfavorable in respect to color reduction. Adsorption of color and oxidative decrease in color are favorable. Oxidative increase in color and oxidative stabilization against adsorption are unfavorable. Adsorbents are shown to catalyze these oxidative reactions.

Under any comparable set of conditions significantly lower colors result when bleaching is carried out under vacuum or in an inert atmosphere. Multiple stage bleaching under atmospheric conditions shows no advantage because of the adverse oxidative effect but may be advantageous under vacuum conditions.

Low pH earths respond better than high pH earths to vacuum bleaching with respect to improved color removal and oil stability.

THE bleaching of vegetable oils with adsorbent materials is not merely a matter of adsorption. Oxidation and possibly other chemical reactions play an important part. It is the purpose of this paper to show the effect of oxidation on bleaching results and to compare atmospheric bleaching with vacuum bleaching using laboratory batch methods. In the latter procedure oxidation is largely avoided.

Published data pertaining to the effect of oxidation on color changes in vegetable oils are rather limited. Bailey (1) states that oxidation has a bleaching effect on the carotenoid pigments but that it tends to develop the color of certain other pigments and in some cases produces colored compounds of a quinoid nature from the fatty acids or glycerides of the oil. He also states that the heating of unbleached oils to a high temperature may cause their color to become set, after which they cannot be bleached. Columbic (2) found that the increase in oil color after prolonged aeration at high temperature was due, in a large extent at least, to the formation of 5-6 quinones from relatively light colored precursors. Odeen and Slosson (3) observed in bleaching sardine oil under atmospheric conditions with activated clay that best results were obtained by contacting the oil and clay for only five minutes before filtration. Higher colors resulted when the contact time was increased. They also observed that better decolorization takes place if the clay is added in a single dose rather than increments and that multiple stage bleaching, under atmospheric conditions, is less effective than single stage bleaching. They attributed these phenomena to oxidation or polymerization or a combination of the two. Robertson, Munsberg, and Gudheim (4) found, in heating refined soybean oil for various periods of time at bleaching temperature before the adsorbent material was added, that the color of the bleached oil increased in proportion to the heating time. They refer to this as the "heat darkening effect" and do not propose a theory to explain it. However, they conclude that the pre-addition of the adsorbent does not, strictly speaking, improve color but inhibits the

effect of heat on bleachability of the oil, which apparently infers heat-stabilization of color against adsorption. Hassler and Hagberg (5) found that the peroxide number of freshly bleached oils is not necessarily indicative of the stability of the bleached oil. They suggested as a possible reason for this that some adsorbents are more selective than others in removing antioxidants and others are more selective in removing the products of oxidation.

Laboratory Procedures. Laboratory bleaches were made in one-liter, three-neck flasks, using a mechanical stirrer. A short piece of glass tubing inserted in a rubber stopper was used as a bearing for the shaft of the stirrer and in vacuum bleaching the gap between the shaft and bearing was sealed with heavy walled rubber tubing lubricated with glycerine. Preliminary experiments indicated that optimum results under vacuum are obtained by evacuating the flask containing the slurry of earth and clay for five minutes at room temperature with agitation, before heating. This procedure was used throughout this work unless otherwise noted. Apparently, practically all of the oxygen that can be removed from the oil-adsorbent slurry at low temperature under these conditions is removed in the first five minutes of evacuation. All oxygen is not removed from the system in this way even after prolonged treatment, as additional gases are evolved after the slurry is heated. Although the optimum bleaching temperature varies with different types of adsorbents, all comparisons were made at a single temperature of 120° C. corresponding to that specified in the A.O.C.S. open cup method of bleaching. Contact time at bleaching temperature was five minutes, and the mixture was cooled as rapidly as possible in a cold water bath to 60° C. before vacuum bleached oil was exposed to the air or open bleached oil was filtered. In vacuum bleaching the pressure was maintained at 2 m.m. or less except during the heating-up period when it rose to a maximum of 10 m.m. due to the evolution of gases.

Effect of Pressure on Color Reduction. Since preliminary tests indicated that most bleaching clays are substantially more effective in vacuum than in atmospheric bleaching, tests were made to determine whether the beneficial effect of vacuum bleaching is due solely to the prevention of oxidation or whether the factor of pressure is involved.

In order to determine the effect of pressure on color reduction as differentiated from the effect of excluding oxygen, samples of refined cottonseed oil were bleached with 1% of activated clay under the following conditions:

1. Exposed to the air under normal atmospheric conditions.
2. At pressure of 1 m.m. Hg.
3. At pressure below 10 m.m. mercury while water vapor was constantly introduced beneath the surface of the slurry.
4. Where the oil-clay mixture was evacuated and nitrogen used to break the vacuum, the oil being then bleached under an atmosphere of nitrogen at atmospheric pressure.

¹ Presented at 22nd fall meeting of American Oil Chemists' Society, Nov. 15-17, 1948, New York City.

5. Where procedure (4) was followed except that nitrogen was introduced vigorously below the oil surface during the contact period, and at atmospheric pressure.

These results, recorded in Table I, show no appreciable difference in bleached oil color using any of the procedures in which oxygen was excluded and show rather conclusively that the beneficial effect of vacuum bleaching is due to elimination of oxidation only.

TABLE I

Treatment	Pressure	Atmosphere	Lovibond Color
Original Oil.....	50Y-7.5R 35Y-4.0R
1. Atmospheric Bleaching.....	Atm.	Air	35Y-2.7R
2. Vacuum Bleaching.....	1 m.m. Hg.	Vacuum	35Y-2.5R
2. Vacuum Water Stripping.....	10 m.m. Hg.	Steam	35Y-2.7R
4. Nitrogen Blanketed.....	Atm.	N ₂	35Y-2.7R
5. Nitrogen Stripped.....	Atm.	N ₂	35Y-2.7R

Effect of Oxidation in General on Color. It can be stated in general that the color of vegetable oil is quite unstable and that the effect of oxidation on color depends on the nature of the pigments present. The color of some oils, such as palm oil, which contain a relatively high concentration of carotene in respect to other pigments, is substantially improved by oxidation. It has been our experience that refined cottonseed and soybean oils may initially increase or decrease in color during early stages of oxidation or heat treatment depending on the quality of the oil. Oil refined from good quality new-crop crude usually decreases, whereas that refined from old-crop crude often increases in color at bleaching temperature. These two types of oil will hereafter be referred to as the non-reverting and reverting types. Data obtained in the laboratory on representative samples of each type of oil, showing original Lovibond color and color after heating the oil for five minutes at 120° C. under atmospheric conditions with mechanical agitation, are given in Table II.

TABLE II

Kind of Oil	Type of Oil	Original Color	Color After Heating 5 Min. at 120° C.
Ref. SBO	Non-reverting	70Y-9.4R	50Y-8.6R
Ref. CSO	Non-reverting	35Y-7.0R	35Y-6.0R
Ref. SBO	Reverting	50Y-8.6R	70Y-9.6R
Ref. CSO	Reverting	35Y-6.4R	35Y-7.1R

In order to determine the effect of oxidation on color increase samples of refined cottonseed and soybean oils of the reverting type were stirred at 100°, 120°, and 130° C. for various intervals of time exposed to the atmosphere and also at pressure of 1-5 m.m. of mercury. In both procedures the oil was rapidly cooled to 50° C. after the heating period and in the latter procedure before the oil was exposed to the atmosphere. Increase in Lovibond red color versus heating time is plotted in Figure 1. These results indicate that oxidation has greater effect on color reversion than temperature. In fact, it is highly probable that the reversion that occurred in the oils heated under vacuum was due to oxidation since some oxygen was obviously present under this condition.

Spectrophotometric data showing per cent transmittance of these oils before and after heating for

25 minutes at 120° C. are plotted in Figure 2. It can be seen from these curves that reversion occurs more or less throughout the spectrum rather than in a definite region.

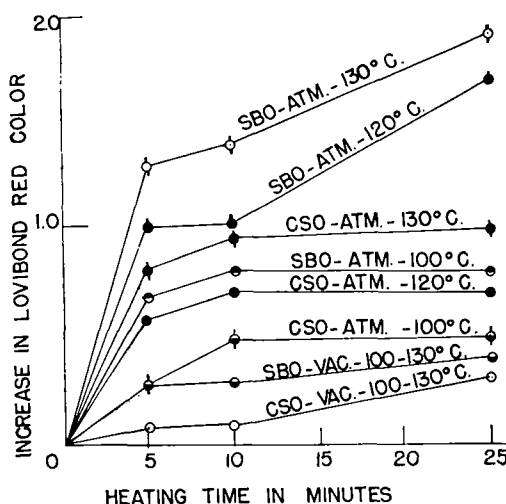


FIG. 1. Heating time vs. increase in Lovibond color of revertible oils.

It would be expected from these results that lower bleached oil colors would be obtained, at least on revertible oils, by bleaching at reduced pressure or in an atmosphere of an inert gas. Since it is more convenient and more practical to bleach at reduced

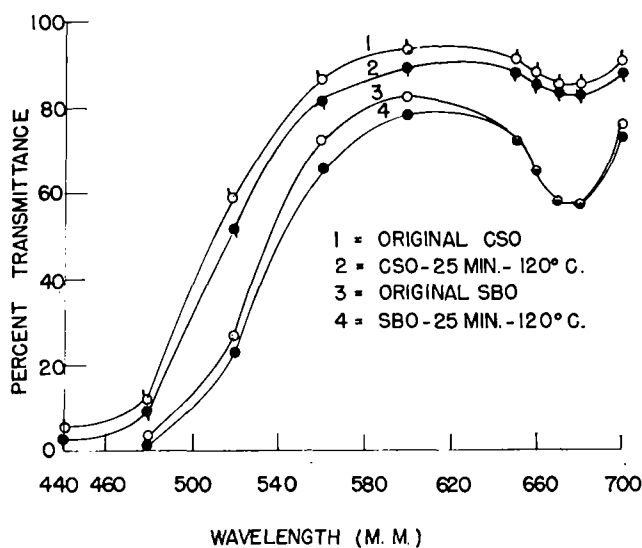


FIG. 2. Color reversion of refined cottonseed oils and soybean oils at 120° C.

(Revertible type oils.)

pressure than in an atmosphere of an inert gas, the former procedure was followed.

Catalytic Effect of Adsorbent on Color Increase. It is reasonable to assume that if oxidation alone was the sole cause of the color intensity changes in existing pigments, the increase in color of a revertible oil heated without adsorbent material under bleaching conditions should represent the maximum improvement in color that could result from vacuum bleach-

ing provided the adsorbent material does not have a catalytic effect on oxidation. In order to answer this question, two revertible type refined soybean oils were studied. Lovibond colors of the untreated and heat-treated portions before and after atmospheric and vacuum bleaching at 120° C. with 2% of an activated clay are given in Table III.

TABLE III

Oil Treatment	Lovibond Color	
	Heated 5 Min.	Heated 2 Hours
Control.....	70Y-9.4R	70Y-8.6R
Heat-Treated.....	70Y-9.6R	70Y-9.2R
Control-Atmospheric Bleached.....	35Y-5.0R	35Y-3.4R
Control-Vacuum Bleached.....	35Y-2.9R	20Y-2.0R
Heat-Treated-Atmospheric Bleached.....	35Y-5.0R	35Y-4.8R
Heat-Treated-Vacuum Bleached.....	35Y-2.9R	25Y-3.0R

One of these oils, with 9.4 red color, increased only 0.2 during the five-minute heating period yet the vacuum bleached oil was 2.1 units lower in color than the atmospheric bleached oil. The other oil, with 8.6 red color, increased 0.6 during the two-hour heating period yet the vacuum bleached oil was 1.4 units lower in color than the atmospheric bleached oil. After pre-heating for two hours, the vacuum bleached oil was lower in color than the original oil atmospheric bleached. These data indicate that the adsorbent had a powerful catalytic effect on oxidation of color. Spectrophotometric curves of the samples with colors given in the second column of Table III are plotted in Figure 3. Here, again, it is shown that the oxidative effect on color occurs more or less throughout the spectrum.

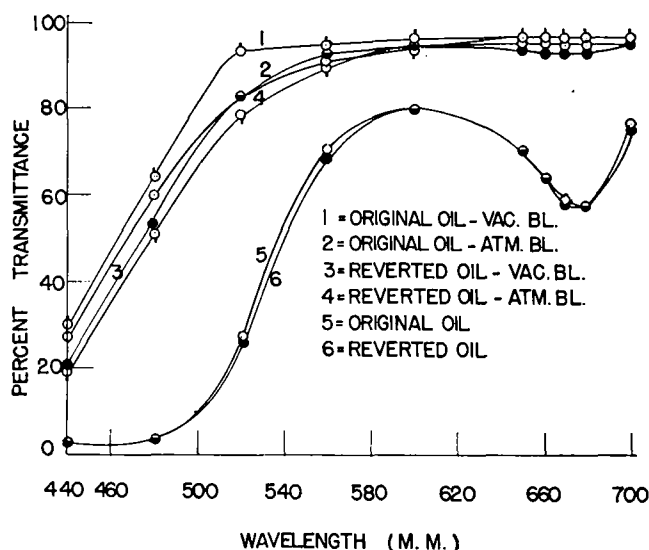


FIG. 3. Spectral transmittance of reverted and non-reverted oil, atmospheric and vacuum bleached.

These results may appear to be at variance with those of previous investigators who found that lower colors are obtained in bleaching if the adsorbent is added to the oil before heating. However, if oxidation tends to render certain pigments less susceptible to adsorption, it follows that adsorbent added to cool oil might advantageously adsorb easily oxidized pigments before they could be stabilized against adsorption through oxidation during subsequent heating.

Effect of Oxidation on Stability Against Adsorption. As previously shown, partial oxidation causes the color to increase in some oils and decrease in others. If vacuum bleaching shows improvement over atmospheric bleaching of oil of the latter type, then oxidation must stabilize color against adsorption and the stabilizing effect must be greater than the overall effect of other oxidative changes in color. Vacuum bleaching has been found to be decidedly effective both on revertible and non-revertible types of oil.

Typical curves showing Lovibond red color versus concentration of natural and activated clay used in atmospheric and vacuum bleaching of non-revertible refined cottonseed and soybean oils are plotted in Figures 4 and 5. Similar data for revertible oils are plotted in Figures 6 and 7. The relative efficiency of each type of clay can be determined at various levels

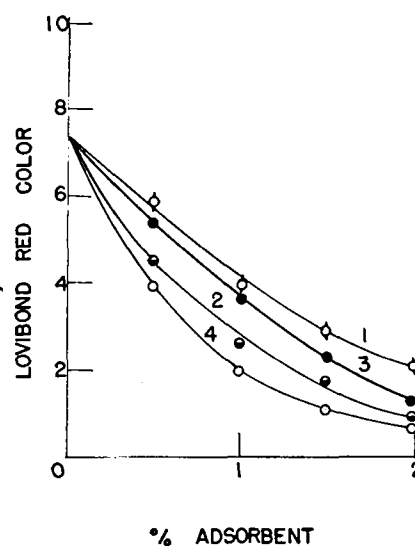


FIG. 4. Vacuum vs. atmospheric bleaching of non-revertible cottonseed oil.

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

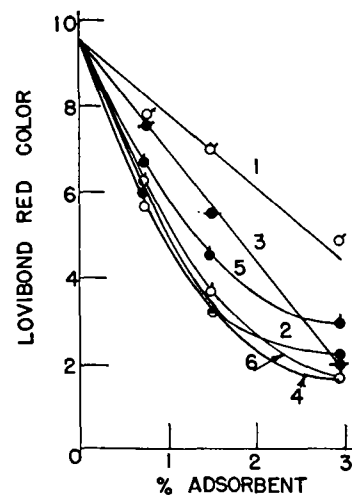


FIG. 5. Vacuum vs. atmospheric bleaching of non-revertible soybean oil.

1. Activated clay (A) used in atmospheric bleaching.
2. Activated clay (A) used in vacuum bleaching.
3. Activated clay (B) used in atmospheric bleaching.
4. Activated clay (B) used in vacuum bleaching.
5. Natural clay used in atmospheric bleaching.
6. Natural clay used in vacuum bleaching.

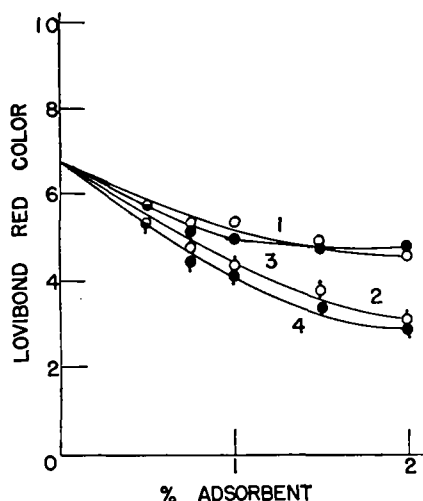


Fig. 6. Vacuum vs. atmospheric bleaching of revertible cottonseed oil.

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

of bleached oil color on these same four oils from adsorption isotherms which are given in Figures 8, 9, 10, and 11.

Effect of Oxidation on Pigment Color Changes. As shown in Figures 8 and 9, points were considerably out of line for some clays used in atmospheric bleaching of non-revertible oils, but data as a whole indicate that the Freundlich equation holds fairly well in bleaching oils of this type. The direct effect of oxidation on color decrease of such oil has not been

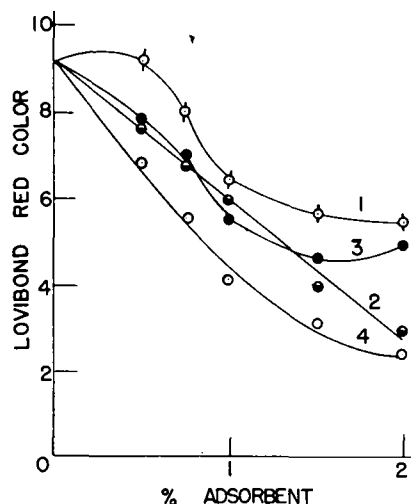


Fig. 7. Vacuum vs. atmospheric bleaching of revertible soybean oil.

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

investigated. However, since the Freundlich equation seems to hold true it appears that temperature rather than oxidation may be responsible for color decrease.

It can be seen from Figures 10 and 11 that the Freundlich equation does not hold true in bleaching revertible oils, but vacuum bleaching tends to straighten out the adsorption isotherm. These data were obtained using a maximum of 3% adsorbent in

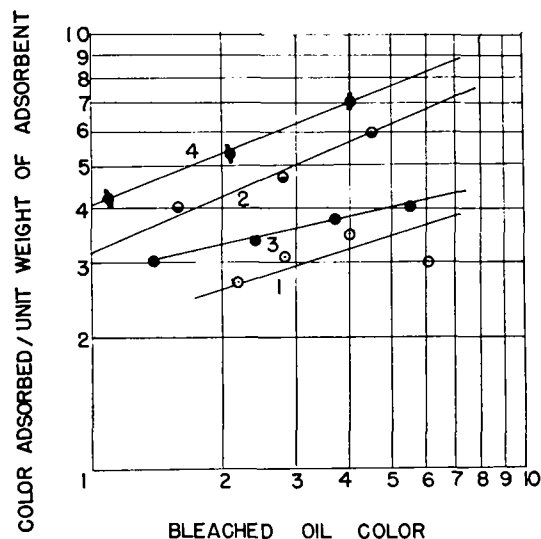


Fig. 8. Adsorption isotherms for bleaching clays used in atmospheric vs. vacuum bleaching of non-revertible refined cottonseed oil.

(Color is expressed in Lovibond red units)

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

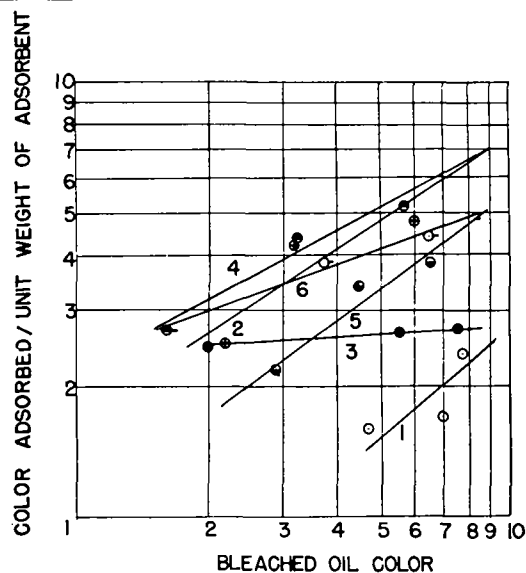


Fig. 9. Adsorption isotherms for bleaching clays used in atmospheric and in vacuum bleaching of non-revertible soybean oil.

(Color is expressed in Lovibond red color.)

1. Activated clay (A) used in atmospheric bleaching.
2. Activated clay (A) used in vacuum bleaching.
3. Activated clay (B) used in atmospheric bleaching.
4. Activated clay (B) used in vacuum bleaching.
5. Natural clay used in atmospheric bleaching.
6. Natural clay used in vacuum bleaching.

the bleach tests. Additional tests were made, using a maximum of 6% adsorbent to obtain more points for the adsorption isotherm which is plotted in Figure 12 for an activated clay used in bleaching a revertible refined soybean oil. Each of these curves shows an adsorption maximum at a definite bleached oil color. As previously shown, oxidation has a net effect of darkening the color of revertible oils and adsorbent materials have a decided catalytic effect on oxidation. It is reasonable to expect that the catalytic effect per unit weight of adsorbent will be greatest at low

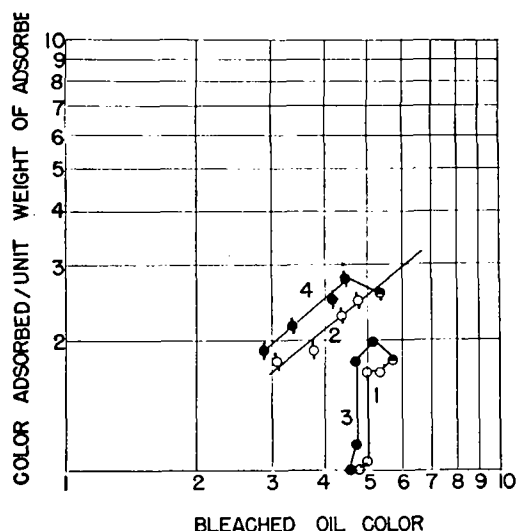


FIG. 10. Adsorption isotherms for bleaching clays used in atmospheric and in vacuum bleaching of revertible cottonseed oil.

(Color is expressed in Lovibond red units.)

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

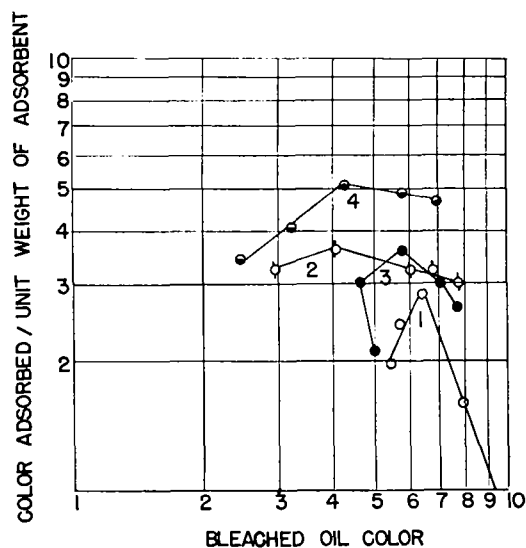


FIG. 11. Adsorption isotherms for bleaching clays used in atmospheric and vacuum bleaching of revertible soybean oil.

(Color is expressed in Lovibond red units.)

1. Natural clay used in atmospheric bleaching.
2. Natural clay used in vacuum bleaching.
3. Activated clay used in atmospheric bleaching.
4. Activated clay used in vacuum bleaching.

concentration of adsorbent and that at any adsorbent concentration an equilibrium exists between color formed through oxidation and color adsorbed. The shapes of the curves shown in Figures 10-12 indicate that this is true. The adsorption isotherm for an ideal non-revertible oil with 10.0 Lovibond red color bleached with an adsorbent which has a capacity of 1 red unit per 1% adsorbent, 2 red units per 2% adsorbent, 3 red units per 3% adsorbent, etc., is designated by the straight line in Figure 13. If it is assumed that this same oil, bleached with the same adsorbent, initially increases in color to 14.0 red due solely to oxidation and calculations for plotting the isotherm are based on the assumption of an initial

color of 10.0, then the isotherm is designated by the curve shown in Figure 13 which is essentially of the same shape as those shown in Figures 10-12 for revertible oils. Therefore, it seems rather certain that the Freundlich equation does not hold true in bleaching revertible oils because of the production of pigments through oxidation. If there is a maximum or peak in the adsorption curve, it can be assumed that pigments have been produced and conversely if there is no peak, then pigments have not been produced. However, the presence or absence of a peak cannot be determined unless sufficient points are obtained at relatively low concentrations of adsorbent.

Counter Current or Multiple Stage Bleaching. If bleaching is strictly a matter of adsorption, it is obvious from the Freundlich equation that better results should be obtained in multiple stage or counter current bleaching than in single stage bleaching. As pointed out by Odeen and Slosson, the reverse of this is true and the reason is no doubt due to the effect of oxidation on color. If all oxidation could be eliminated, then lower colors should be obtained with a multiple stage procedure. A comparison was made between single and dual stage atmospheric versus vacuum bleaching of a revertible soybean oil using an activated clay. A 2% clay was used in single stage, and two increments of 1% clay in dual stage bleaching. The oil was cooled to 60° C. and filtered before the second increment was added. Results of these tests are given in Table IV.

In both open and vacuum procedures better results were obtained in single stage bleaching. However, in

TABLE IV

Bleach Procedure	% Clay Used	Lovibond Color
Control.....	None	70Y-8.7R
Atmospheric.....	2	25Y-4.8R
Atmospheric.....	1	25Y-5.6R
Atmospheric.....	1+1	25Y-5.5R
Vacuum.....	2	20Y-2.9R
Vacuum.....	1	25Y-3.8R
Vacuum.....	1+1	20Y-3.1R

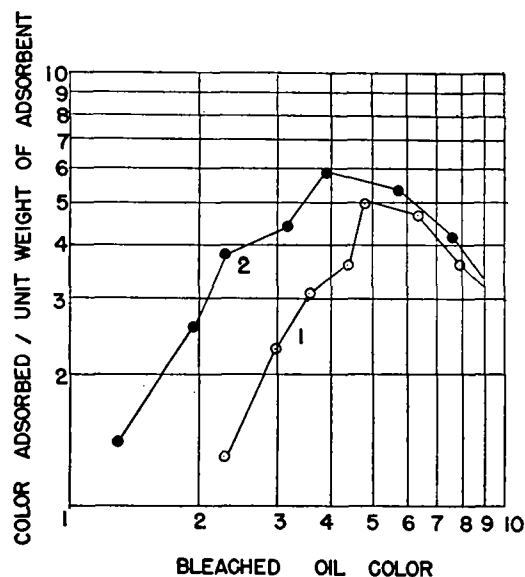


FIG. 12. Adsorption isotherms for activated clay used in atmospheric vs. vacuum bleaching of revertible soybean oil.

(Color is expressed in Lovibond red units.)

1. Atmospheric bleached.
2. Vacuum bleached.

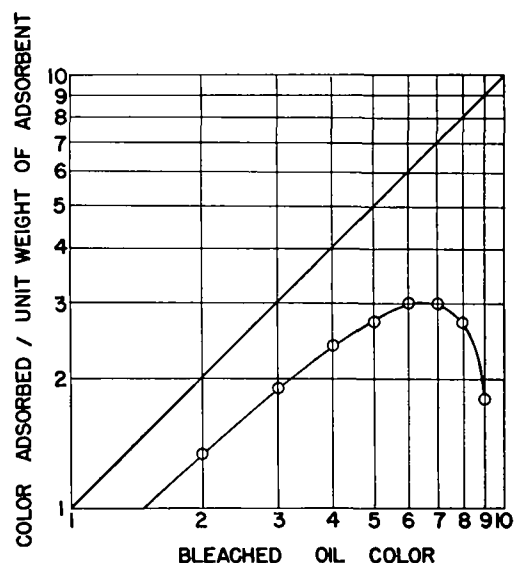


FIG. 13. Effect that oil color increase in bleaching would have on the shape of the adsorption isotherm, calculated on the basis of original oil color.

vacuum bleaching the difference was very slight, and it is highly probable that if all oxygen had been eliminated, better results would have been obtained in dual stage bleaching. It was toward the end of the oil season when these tests were made and high quality non-reversible oils were not available, and we do not have similar data on oils of this type. However, it seems likely that multiple stage bleaching may be significantly advantageous on such oils.

Variability of Response to Vacuum Bleaching. The extent of improvement in bleached oil color due to vacuum bleaching depends upon the nature of the oil, type, and concentration of adsorbent used. Cottonseed and soybean oils have been classified in two groups comprising those oils which increase and those which decrease in color on mild oxidation. Actually the two groups overlap, and it would seem most unlikely that oxidation would have exactly the same effect on color of any two oils from different sources. It would be expected that greater improvement should result in vacuum bleaching of highly reversible oils because the direct effect of oxidation as well as the stabilizing effect on color is decidedly significant, but this has not been proved. We have tested a large number of natural and activated clays and activated carbons in vacuum versus atmospheric bleaching and the activated clays were found to show the greatest response to vacuum bleaching. One of the natural clays and all of the activated carbons showed no significant improvement due to vacuum bleaching. It is possible that the reason some adsorbent materials give poor response to vacuum bleaching is that they may be equally selective in adsorption of oxidized and non-oxidized pigments. It is also possible that oxygen is bound so strongly to some adsorbents that it is not released to a great extent at reduced pressure.

Theory Developed From Laboratory Work. In bleaching oils with adsorbents an equilibrium exists between two favorable and two unfavorable conditions. The favorable conditions are adsorption of color by the adsorbent material and decrease in color of certain pigments due to heat and/or oxida-

tion. The unfavorable conditions are color increase due to oxidation and stabilization of color against adsorption due to oxidation. This may be summarized by the following hypothetical relationship:

$$E = A + (C - B) - D$$

Where:

- E = bleaching efficiency
- A = color adsorbed
- C = color decrease due to heat and/or oxidation
- B = color increase due to oxidation
- D = stabilization of color due to oxidation.

In bleaching high quality oils with the most commonly used adsorbents, D is greater than (C-B). In bleaching low quality oils B is greater than C. In either case improved results are obtained when oxidation is minimized during bleaching.

Effect of Vacuum Bleaching on Oil Stability. When vegetable oils are bleached with an adsorbent material, the peroxide number of the oil tends to increase due to oxidation and, on the other hand, tends to decrease due to selective adsorption of the products of oxidation by the adsorbent material. Thus an equilibrium is established between formation and adsorption of peroxides. Whether the peroxide number of the bleached oil will be higher or lower than that of the original refined oil depends entirely on type and concentration of adsorbent used. Usually at low concentration of adsorbent oxidation is predominant and there is an increase in peroxide number while at high concentration adsorption is predominant and there is a reduction in peroxide number. Results obtained in vacuum versus atmospheric bleaching of identical refined soybean oil are shown in Table V.

TABLE V

Kind of Adsorbent	Peroxide Number		
	% Adsorbent	Atmospheric Bleached	Vacuum Bleached
Control.....	None	4.0	4.0
Activated Clay (1).....	0.75	10.4	4.6
Activated Clay (1).....	1.5	4.0	0.8
Activated Clay (1).....	3.0	1.8	0.8
Activated Clay (2).....	0.75	6.2	4.0
Activated Clay (2).....	1.5	2.0	0.7
Activated Clay (2).....	3.0	.4	0.6
Natural Clay (1).....	0.75	11.0	8.2
Natural Clay (1).....	1.5	8.8	5.7
Natural Clay (1).....	3.0	4.8	2.0
Natural Clay (2).....	0.75	4.4	1.8
Natural Clay (2).....	1.5	1.4	0
Natural Clay (2).....	3.0	0.9	0

As pointed out by Hassler and Hagberg, the initial peroxide number of a bleached oil is not necessarily indicative of the stability of the oil to further oxidation. The reason for this is no doubt due to the fact that residual peroxide number is not necessarily an indication of the degree of oxidation that occurs during bleaching but depends to some extent on the selectivity of the adsorbent in removing products of oxidation. Thus, an adsorbent material that is most selective in adsorbing peroxides may also have greatest catalytic effect on oxidation. However, vacuum bleaching should have no effect on the adsorbent in regard to adsorption of peroxides, and lowering of peroxide value due to vacuum bleaching can probably be attributed to reduced oxidation of the oil. Since vacuum bleaching does have a decided lowering effect on residual peroxide value, it would be expected that oil stability should be improved by vacuum bleaching. Each sample of bleached oil listed in Table 5

was stored at 90° F. in diffused light for a period of two months, and peroxide values were determined at periodic intervals. Average peroxide value of all atmospheric bleached and all vacuum bleached samples at each interval are shown in Figure 14.

TABLE VI

Type of Adsorbent	% Adsorbent	Average Reduction in Oil Stability in Bleaching	
		Atmospheric	Vacuum
Activated Carbon.....	.125-.75	24	21
Natural Clay.....	1	27	22
Activated Clay (1).....	1	25	10
Activated Clay (2).....	1	27	12

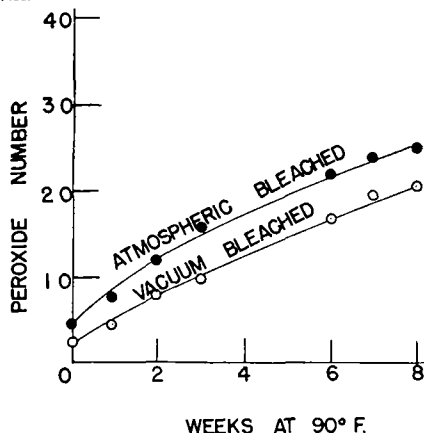


FIG. 14. Effect of vacuum bleaching on oil stability.

Averages for a relatively large number of tests show that stability of vacuum bleached oil, as determined by the Swift Stability Method, is approximately 15% greater than of atmospheric bleached oil when activated clays are used as the adsorbent. Data comparing

the effects of various adsorbents in vacuum versus atmospheric bleaching on Swift Stability of a good quality refined cottonseed oil are given in Table VI.

These data substantiate previous conclusions that the effectiveness of vacuum bleaching depends on the extent to which oxidation is reduced. The activated clays, which showed greatest response to vacuum bleaching in regard to color removal, also showed the greatest improvement in oil stability due to vacuum bleaching. The activated carbon which reduced oil stability only slightly more in atmospheric than in vacuum bleaching showed no significant advantage in vacuum over atmospheric bleaching in regard to color removal.

Summary

In bleaching fatty oils an equilibrium exists between two reactions favorable and two unfavorable in respect to color reduction. Adsorption of color and oxidative decrease in color are favorable. Oxidative increase in color and oxidative stabilization against adsorption are unfavorable. Adsorbents are shown to catalyze these oxidative reactions.

Under any comparable set of conditions significantly lower colors result when bleaching is carried out under vacuum or in an inert atmosphere. Multiple stage bleaching under atmospheric conditions shows no advantage because of the adverse oxidative effect but may be advantageous under vacuum conditions.

Low pH earths respond better than high pH earths to vacuum bleaching with respect to improved color removal and oil stability.

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Directed Interesterification in Glycerides. Reaction in Presence of Added Glycerol

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WHEN triglycerides are heated to a temperature sufficiently high, a process of ester-ester interchange occurs which allows the acid radicals to change places until, at equilibrium, the composition of the triglyceride mixture approximates the composition corresponding with random distribution of the acid radicals in the esters.

At low temperature, in the presence of highly active catalysts, triglycerides can undergo a process of directed interesterification in which fractional crystallization of the triglycerides take place simultaneously with ester-ester interchange (1, 2). The simple form of this process as applied to a fat such as cottonseed oil, containing mixed glycerides of saturated and unsaturated fatty acids, consists of mixing the oil with catalyst and holding the mixture at temperatures below those at which the fully saturated triglycerides, at their equilibrium concentration, can

remain in solution. Crystallization of saturated glycerides from the mixture alters the composition of the reacting phase and allows additional quantities of saturated triglycerides to form progressively from mixed saturated-unsaturated glycerides as new equilibria are approached. In this way a large proportion of the saturated fatty acids of the fat can be segregated into the fully saturated glyceride fraction. The range of triglyceride compositions attainable by interesterification of a given fat is thus greatly extended in comparison with that produced by high-temperature reaction.

This paper describes results that can be obtained when the process is applied to glyceride mixtures containing free hydroxyl groups. When these are present, as in the case when a small proportion of glycerol is added to a triglyceride mixture while it is undergoing interesterification, the process becomes a mixed process of ester-alcohol interchange together with ester-ester interchange since the same catalysts serve to accelerate both these reactions. The ester-

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