

In an effort to verify that absorption at 1.46 and 2.07 μ is proportional to peroxide content, a study of the thermal decomposition of methyl oleate hydroperoxide was made. A sample of methyl oleate hydroperoxide, P. V. = 5,110, was divided in eight portions and sealed in vacuum ampoules. The ampoules were placed in a flask of water, which was allowed to boil under reflux. At appropriate intervals ampoules were removed, the peroxide values were determined, and the near-infrared spectra were measured. The effect of thermal decomposition upon the spectral absorption is shown in Figure 4. The extinction at 2.07 and 1.46 μ diminished linearly with the decrease in iodometric peroxide value. However hydroxy substances (1.42 μ) increased as the peroxides were decomposed.

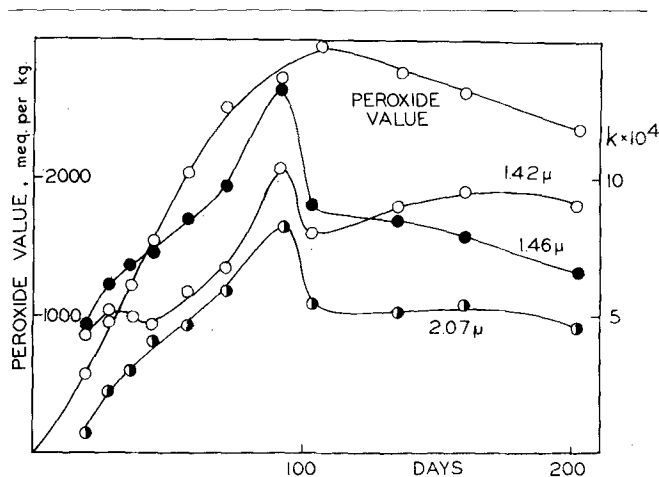


Fig. 5. Autoxidation of methyl linoleate at room temperature.

When a sample of methyl linoleate was allowed to oxidize in air, the extinction at 1.46 and 2.07 μ increased in parallel fashion (Figure 5). Hydroxyl absorption (1.42 μ) likewise increased as the peroxide value increased. When maximum peroxide value was attained, discontinuities in the curves for absorption at 1.42, 1.46, and 2.07 μ were observed. Thereafter, as iodometric peroxide values decreased slowly, hydroperoxide absorption at 1.46 and 2.07 μ decreased slowly whereas hydroxyl absorption at 1.42 μ increased, indicating peroxide decomposition.

The detection and measurement of hydroperoxides by their absorption at 2.82 μ is possible by use of conventional infrared spectrophotometers, but resolution by rock salt prisms in that region is poor, making it difficult to differentiate between the hydroperoxide maximum at 2.82 μ and the hydroxyl maxi-

mum at 2.77 μ . Some advantage may be gained by the use of a quartz prism, but the region of 2.7–2.9 μ is the location of absorption maxima of aldehydes, ketones, acids, and esters as well as hydroxyls and hydroperoxides. For this reason the present study centered on the maxima at 1.46 and 2.07 μ , which are sufficiently removed from other absorption maxima to make interference least likely. In these two selected regions the resolution of the quartz prism is sufficient to distinguish the neighboring O-H and OO-H absorptions. A disadvantage is that these maxima are not expressions of the fundamental modes of vibration. The maximum at 2.07 μ is probably a combination absorption and that at 1.46 μ is a harmonic of the fundamental mode at 2.82 μ . Consequently these absorptions are of low intensity, and they must therefore be measured in high concentrations or in long cells. The solutions used in measurements reported here varied between 3 and 10% in carbon tetrachloride. The measurement of most of the spectra required 100 to 200 mg. of sample. This can be a limiting factor in chemical studies. In the present investigation hydroperoxides could not be detected by spectra until the peroxide value was about 500 meq./kg. Detection of lower concentrations is possible with cells of longer light path.

Summary

Near-infrared spectra have been measured on a group of hydroperoxides of fatty acid esters and related substances. Only those substances having an -OOH group were found to absorb at 1.46 and 2.07 μ . Dialkyl peroxides and ozonized unsaturated substances had no such maxima in their near infrared spectra although they had high iodometric peroxide values. In a study of the thermal decomposition of methyl oleate hydroperoxide and a study of the autoxidation of methyl linoleate, the intensity of absorption at 1.46 and 2.07 μ paralleled the iodometric peroxide value.

Acknowledgment

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The Bleaching of Soybean Oil. A Spectrophotometric Evaluation

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THE QUANTITATIVE STUDY of bleaching agents and/or methods requires information on the amount of coloring matter in the initial and partially decolorized oil. Since the eye is an integrating organ, similar color responses can be caused by different

compositions of pigmentation. Lovibond glasses numerate what the eye sees and hence are not suited for determining the amounts of the different pigments. Spectrophotometric evaluation was chosen because of the intrinsic suitability of this method and the availability of good instruments.

¹ Now with E. I. du Pont de Nemours Company Inc., Kinston, N. C.

During the past 11 years nine papers have been published in this journal (or in Oil and Soap), in which the bleaching of soybean oil has been discussed (1, 2, 4, 5, 7, 8, 9, 10, 11). Seven of these papers contained spectrophotometric data while the other two papers (1, 7) expressed the results in the Lovibond color system. In four of the papers (1, 4, 9, 11) adsorption isotherms were used in comparing the decolorizing agents, and all except one (1) determined the color spectrophotometrically. Two of these papers (4, 9) presented isotherms for the adsorption of the green pigment.

In the present work the efficacy of the decolorizing agents is based on the reduction of the absorbances ($-\log T/T_0$) at 455 millimicrons and 665 millimicrons (or at the position of the maximum), respectively. For soybean oil the former wavelength is the position of the largest of the absorption maxima for the carotenoids, the yellow pigments, and the latter wavelength is the position of the largest of the absorption maxima for pheophytin-A, the green pigment (see reference 8 for the spectra of pheophytin and chlorophyll). The reddish color of some soybean oil may be due to the strong end-absorption of the carotenoids, which extends into the green portion of the visible spectrum. The degradation of pheophytin-A may also contribute to this reddish color.

Experimental Procedure

Bleaching Procedure. A two-liter, three-necked flask equipped with thermometer and stirrer was used to hold the kilogram sample of soybean oil. The sample was heated to 170°F. as rapidly as possible (465-watt Glascol hemispherical heating mantle, voltage regulator set at 110 volts), the decolorizing agent added, the pressure reduced to less than one inch of mercury, and the timer started. At an oil temperature of 208°F. the voltage regulator was set at 26-28 volts, and the temperature became constant at 220°F. Thirty minutes (for most of the samples) after adding the decolorizing agent, the vacuum was released and 25 g. of filter aid were added, followed by filtration with suction. This will be referred to as regular bleaching.

Pressure Bleaching. This was done under nitrogen with the Parr Pressure Apparatus (Series 4500). The filter aid was added with the decolorizing agent and filtration made directly from the pressure chamber or after bleaching the pressure was reduced, then the oil was poured into a beaker containing the filter aid, followed by filtration with suction.

Measurement of Absorbance. All measurements were made on undiluted oil versus cyclohexane with a Beckman Model DU spectrophotometer. Ten-, five-, and one-centimeter cells were used. Two-way quartz inserts were employed with the one-centimeter cells for obtaining one- or three-millimeter paths for samples having absorbances greater than one.

Materials. Special Filtrol (designated as F), an activated clay absorbent manufactured by the Filtrol Corporation. Neutral Earth (NE), a natural clay prepared by Bennett-Clark, as an official natural bleaching earth for the A.O.C.S. Acid Clay (AC), a special bentonite clay manufactured by the Magnet Cove Barium Corporation. Darco S-31 (D), an activated carbon manufactured by the Chemicals Division of the Atlas Powder Company. Nuchar CEEN

(NC), an activated carbon manufactured by the Industrial Chemical Sales Division of the West Virginia Pulp and Paper Company. Dicalite 4200, a filter aid manufactured by the Dicalite Division of the Great Lakes Carbon Corporation. Cyclohexane, Eastman or Phillips Spectro Grade.

Results and Discussion

Data for Typical Oils. Table I lists the absorbances ($-\log T/T_0$) for several alkali-refined oils ("N") and the acetic anhydride water degummed oils ("50" oil) (U. S. Pat. 2,754,309). It is seen that the median absorbance of the "50" oil at 670 millimicrons in a 10-centimeter cell would be 2.7 although the actual measurement was 0.278, using a one-centimeter cell. These results are typical for the oils used in this study.

TABLE I
Absorbances of Unbleached Oils $\times 1,000$

	"N"		"50"	
	Yellow	Green	Yellow	Green
	(1 mm.)	(10 cm.)	(1 mm.)	(10 cm.)
No. samples.....	4	14
Median.....	1095	2095	1335	2780
Highest.....	1150	2340	1380	3320
Lowest.....	930	1830	1280	2280

Effects of Time and Temperature. In order to determine the sensitivity of laboratory bleaching to time and temperature, two decolorizing agents were used at the 1.2% level on "50" oil samples. The results given in Table II indicate that good contact was not established until after about 20 min. Thirty minutes were chosen as a satisfactory time since good dispersal of the decolorizing agent is assured, and more than 95% of the color is removed. Although the highest temperature used was the most effective from a color removal standpoint, 220°F. was chosen as being more typical of plant practice.

TABLE II
Effect of Time and Temperature.
Absorbances of Yellow and Green Pigments ($\times 1,000$)

	Time	Activated Clay (F)		Natural Clay (NE)	
		4550	6550	4550	6550
		(1 cm.)	(10 cm.)	(1 cm.)	(10 cm.)
(125°F.)	10 min.	2880	650	7220	1110
	20	2730	514	7070	1080
	40	1860	334	6460	940
(220°F.)	10 min.	1180	163	4490	546
	20	1180	134	3670	526
	40	796	114	3580	475
(265°F.)	10 min.	566	125	2520	456
	20	471	114	2360	454
	40	356	081	1970	454

The Isotherms. The Freundlich equation was used in the form:

$$\log [(A_0 - A_x)/g] = \log K + N \log A_x, \text{ where}$$

A_0 = absorbance of original oil,

A_x = absorbance of oil after bleaching,

g = grams of decolorizing agent used for one kilogram of oil, and

K, N = constants.

A plot of $(A_0 - A_x)/g$ against A_x on logarithmic paper results in a straight line (at least for some range of $A_0 - A_x$). In the case of the yellow pigment the absorbance is expressed for a one-millimeter path

and for the green pigment the absorbance is expressed for a 10-centimeter path, and all values are multiplied by 1,000. The decolorizing action toward the green pigment in "50" oil for the bleaching agents is shown in Figure 1. Estimated best lines were drawn through the experimentally determined values without extrapolation. The number of experimentally determined points ranged from 10 to 40 for each decolorizing agent used.

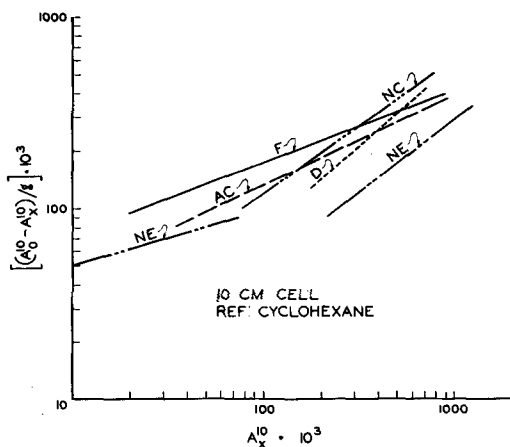


Fig. 1. Adsorption isotherms for the removal of green pigment from "50" oil by regular bleaching.

- AC = Acid Clay, a special bentonite clay.
- D = Darco S-31 brand activated carbon.
- F = Special Filtril brand activated clay.
- NC = Nuchar CEEN brand activated carbon.
- NE = Neutral Earth brand natural clay.

In this and the following four figures the abscissae are proportional to the amount of color in the oil after bleaching, and the ordinates are proportional to the amount of color removed by 1 g. of decolorizing agent.

In the case of natural clay (NE) it was evident that a single isotherm could not represent all the data, and two separate best lines were drawn as shown. From Figure 1 it can be calculated that to bleach a "50" oil having an initial absorbance of 2.2 (at 655 millimicrons or at position of maximum) to a final value of 0.070 (for a 10-centimeter path) would require 1.4% of activated clay (F) or 2.4% of natural clay (NE).

Figure 2 shows the results for the removal of

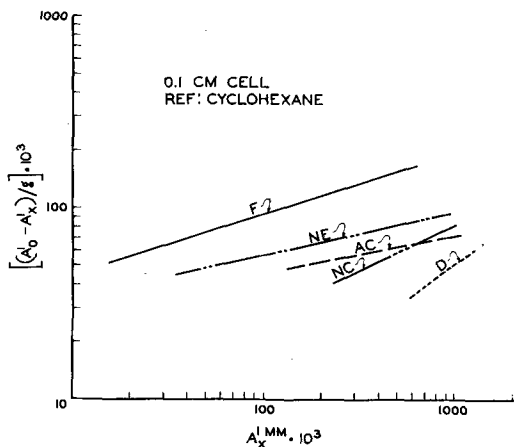


Fig. 2. Adsorption isotherms for the removal of yellow pigment from "50" oil by regular bleaching.

yellow pigment from the same "50" oil. It is now seen that the activated carbons are relatively more effective toward the green pigment than toward the yellow. A comparison of the special bentonite clay (AC) with natural clay (NE) shows a reversal of their relative effectiveness for the two kinds of pigments. These differences in the action of the decolorizing agents can be determined most easily by spectrophotometric measurements at the two wavelengths used in this work.

It is generally known that the deodorization of an unbleached soybean oil results in a product with a most unacceptable greenish color. Table III contains spectrophotometric data for a typical case. Because of the relatively high heat stability of the green pigment the emphasis in bleaching should be on the removal of this pigment. This emphasis was followed in the laboratory work.

TABLE III
Effect of Deodorization. Absorbances of "50" Oil \times 1,000

	Yellow (1 mm.)	Green (10 cm.)
Before.....	13300	2200
After.....	123	1800
Percentage of decrease.....	99	18

The Effect of Pressure. Figure 3 shows the results for bleaching under pressure. Curve (F) of Figure 1 is shown for comparison. It is seen that bleaching under pressure followed by filtering under pressure is an aid to color removal (compare curves A and B). This result is consistent with the fact that plant bleaching is more efficient than laboratory bleaching.

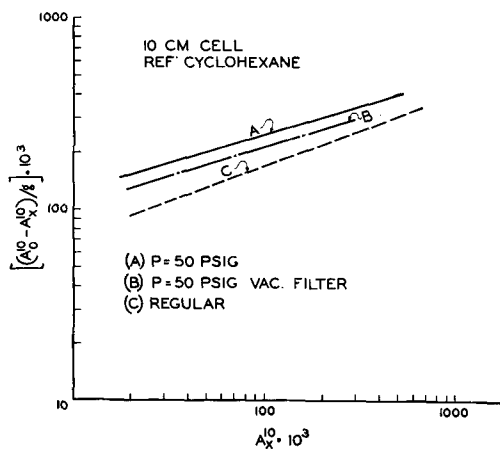


Fig. 3. Adsorption isotherms for the removal of green pigment from "50" oil by pressure bleaching. Curve (C) is the same as F in Figure 1.

Comparison of "N" with "50" Oil. Two different batches of "N" oil were bleached with activated clay (F) with amounts varying from 0.4% to 1.8% (in steps of 0.1% and/or 0.2%). In plotting the data it became apparent that the scatter of points indicated separate isotherms for the two batches. Such was not the case for different batches of "50" oil. These results are shown in Figures 4 and 5. From the latter it is seen that the yellow pigments were removed more easily from "N" than from "50" oil. The different isotherms for the "N" oils probably

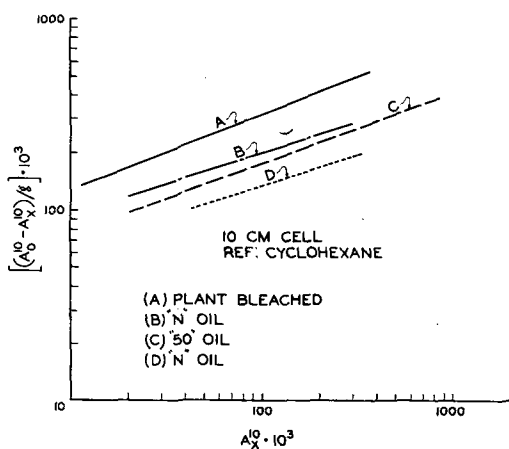


FIG. 4. Adsorption isotherms for the removal of green pigment from two different batches of "N" oil and from "50" oils by regular bleaching.

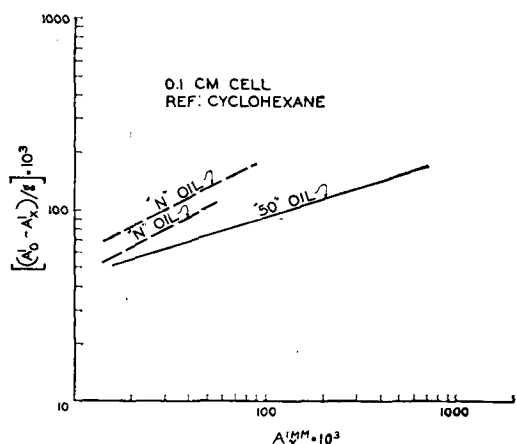


FIG. 5. Adsorption isotherms for the removal of yellow pigment from two different batches of "N" oil and from "50" oils by regular bleaching.

indicates the difficulty in maintaining optimum control in the alkali refining of soybean oils.

Plant Bleached Oils. The median absorbances for 14 "50" oils and 12 plant-bleached "50" oils (using Special Filtrol brand activated clay) were used to calculate one point, through which a line was drawn parallel to the isotherm for laboratory bleached "50" oil as shown in Figure 4. Using this estimated isotherm, a bleaching chart was prepared as shown in Figure 6. It follows from the Freundlich equation that the slopes of these lines should vary inversely as the equilibrium color (A_x), and this is seen to be the case. Knowing the absorbance (10-cm. cell) of the green pigment in a "50" oil entering a bleaching vessel (for example, $A_0 = 2800$) and supposing that a bleached oil of 100 units ($=A_x$) is required, it fol-

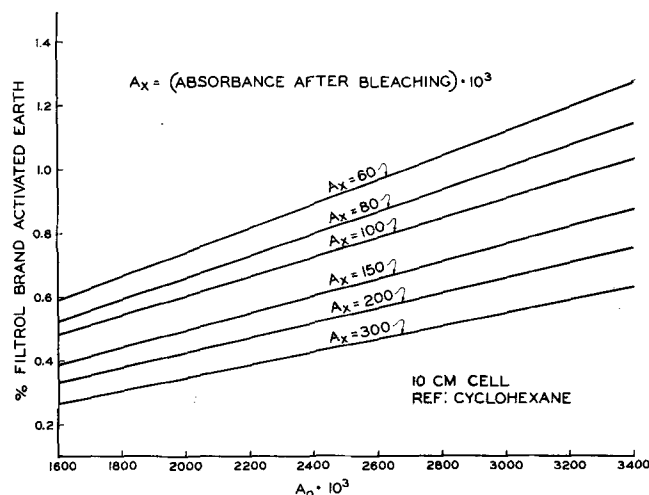


FIG. 6. Bleaching chart for the removal of green pigment from "50" oil. Plant bleaching using Special Filtrol brand activated clay.

lows from the chart that a 0.85% bleach, using activated clay (F), would be necessary.

Summary

Bleaching results are evaluated spectrophotometrically by measuring the change in the absorbances at 455 and 670 (or 665) millimicrons, respectively. Three bleaching clays (one was activated) and two activated carbons were used for decolorizing soybean oils made break-free by either alkali refining or acetic anhydride water degumming. Bleaching times varied from 10 to 40 min. with 30 min. being used in the evaluations. Although bleaching at a temperature of 265°F. removed more color than bleaching at 125° or 220°F., the latter temperature was used in this study. Most of the bleaching was done under vacuum although using a nitrogen pressure of 50 p.s.i.g. removed more color. Results are expressed by Freundlich isotherms, and a bleaching chart for the control of plant bleaching is given. It is shown that in the bleaching of soybean oil primary consideration should be given to the removal of green pigment.

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Solubilization—A Micellar Phenomenon

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AN UNUSUAL PHENOMENON associated with dilute surfactant solutions is their ability, in a micellar state, actually to solubilize water-insoluble substances. McBain (48) defined solubilization as the spontaneous passage of molecules of a substance

insoluble in water into a dilute aqueous solution of a surfactant to form a thermodynamically stable solution.

Micelles, as regular aggregations of molecules, appear in aqueous and nonaqueous media. The present