"The Rapid Determination of Moisture Content with Especial Reference to Oil Seeds and Their Products," by E. B. Freyer, Buffalo, N. Y.

Report of Standards Committee—M. F. Lauro, Chairman, New York City.

"Ouricury Palm Kernel Oil," by G. S. Jamieson, Washington, D. C., and R. S. McKinney, Washington, D. C.

Report of Stability Committee—L. B. Kilgore, Washington, D. C.

"Pressing Cottonseed Meats in the Expeller which have been cooked under Pressure," by R. H. Pickard, Cleveland, Ohio.

Report of Fat Analysis Committee—R. C. Newton, Chairman, Chicago, Ill.

"Absorption Spectra of the FAC Color Standards," by W. M. Urbain and H. L. Roschen, Chicago, Ill.

Report of Referee Board—A. S. Richardson, Chairman, Ivorydale, Ohio.

"Composition of a Soybean Oil of Abnormally Low Iodine Value," by F. G. Dollear, P. Krauczunas and K. S. Markley, Urbana, Ill.

Report of Sulphonated Oil Committee—R. Hart, Chairman, New York City, N. Y.

Report of Soap in Oil Committee—E. H. Harvey, Chicago, Ill.

Report of and Joint Meeting with Chemists' Committee of the National Cottonseed Products Association, by T. C. Law, Atlanta, Ga.

Report of Uniform Methods and Planning Committee—J. J. Vollertsen, Chairman, Chicago, Ill.

Special Committee Reports.

Miscellaneous Business.

Report of Nominating Committee—E. C. Ainslie, Atlanta, Ga.

Election of Officers.

Announcements.

Adjournment of Technical Meeting.

Banquet and Dance—Southern Yacht Club.

Saturday, May 14th, 1938

Trip. Port Sulphur Mines, fee $1.00.

* * *

NOTES

President Sheely has named Messrs. E. C. Ainslie, W. D. Hutchins, and A. A. Robinson as members of the Nominating Committee. Mr. Ainslie will act as Chairman.

The banquet and dance at the Southern Yacht Club on Friday evening promises to be more delightful than ever. Music will be supplied by Leslie George's Orchestra, well-known New Orleans musicians.

THE INFLUENCE OF BLEACHING ADSORBENTS ON THE STABILITY OF EDIBLE OILS

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Abstract

In order to provide oils light in color and free of objectionable odor, it is generally necessary to process them with various adsorbents such as fuller's earth, activated clay, and activated carbon. While this treatment furnishes a more desirable product in keeping with the taste of the American public, unfortunately, it sometimes results in leaving the oil more susceptible to the development of rancidity later on. This work is a study of the effect of various adsorbents, and while it does not provide any final conclusions, it does indicate that the resulting rancidity can be controlled to a large extent by the selection of the proper adsorbent.

Edible oils to be palatable and salable must be light in color and of good flavor and odor. Three processes, refining, bleaching, and deodorization are employed to meet these requirements. These processes are frequently believed to lower the resistance of the oil to deteriorative oxidation and subsequent rancidity. It is generally accepted that a crude vegetable oil is more stable than the corresponding refined oil.[1] During caustic refining, natural anti-oxidants existing in the crude oil (such as phosphatides) are removed, thus lowering the resistance of the oil to oxidation. During the bleaching operation, the pigments, e.g., carotene, chlorphyll, xanthophyll, are removed; it is generally believed that these too have definite anti-oxidant properties,[2] although conflicting data has been found on this.[3]

There are essentially three classes of adsorbents used in bleaching vegetable oils; namely, natural earths, activated earths, and activated carbons. For economic maximum bleach a carbon-earth mixture is generally employed, the ratio of carbon to earth depending on the type of oil. The chief factors influencing the oil refiner in choosing the type of adsorbent have been a maximum bleach and a minimum oil retention. It is only in recent years that attention has been given to stabilizing vegetable and especially animal oils. Although refined bleached vegetable oils do not oxidize readily to the rancid point, they do oxidize quite readily to a point of color reversion. The oil refiner must be careful that his choice of adsorbent does not accelerate this, for an oil loses its salability when it darkens.

The scope of our work was to bleach cottonseed oil with various concentrations of different adsorbents and then chart the quality of the oil by chemical and physical tests through an induction period. We have not been able to find a limiting definition of induction period, but we understand it to be the period of time under which an oil is maintained under controlled conditions up through the point of definite rancidity. The first step was the selection of one of the methods that have been devised for accelerated oxidation of edible oils. For our purposes the incubation oven method similar to that of

Schaal[4] was found the best for, although slow, it gave more consistent checks than we were able to obtain with the more accelerated tests.[5] By this method, a small sample of oil is placed in a beaker exposing a great surface of the oil to atmospheric oxidation. The beakers are then placed in a ventilated incubator at 60° C. and withdrawn when desired for testing.

The next step was the selection of a method of measuring the amount of oxidation. Oxidation in the oil molecule has been found to be accompanied by an increase in free fatty acid content. Substances such as ethers, ketones, lactones, aldehydes are formed first; on further oxidation free fatty acids are formed. An F.F.A. test might give an indication of oxidation, but this is not necessarily so, for, when moisture is present, it may cause hydrolysis of the glyceride, giving rise to an increase in free fatty acid content. Therefore, this test is of little value as a quantitative measure of oxidation.

Wheeler,[6] who has done much work on the stability of cottonseed oil, has shown that as the oil oxidizes the iodine value drops. It is believed that during the oxidation, the double bonds being saturated with oxygen break down, resulting in a drop in iodine value. However, the iodine value does not drop at a rate corresponding to the increase in oxygen absorption.

The Kreis Test[7] has been employed by oil refiners for many years as a means of checking the quality of an oil. When a 1% solution of ethereal phloroglucinol is added to an oil-concentrated hydrochloric acid mixture, a pink to red color develops depending on the extent of the supposed oxidation of said oil. [The theory is that this red color is formed by the action of phloroglucinol of epihydrin aldehyde which is usually associated with the presence of heptylic aldehyde in the oil. This heptylic aldehyde is known to have a vile smell and supposedly causes the rancid odor.[8]] However, it has been shown that this test becomes positive long before organoleptic rancidity appears.[9] We would emphasize that we are not condemning the Kreis Test, for it serves the purpose of giving the oil refiner an indication as to the quality of his oil.

The "Peroxide Value"[10] gives a quantitative measure of oxidation up through the point of organoleptic rancidity. In this test the loosely held oxygen taken up at the double bond linkages liberates iodine from potassium iodide. Although satisfactory for measuring oxidation, this test does not denote the point of organoleptic rancidity. This is because the amount of oxygen required to develop rancidity depends on the type of oil. As an example, lard, to become organoleptically rancid does not need to take on nearly as much oxygen as cottonseed oil. Also the rate of oxidation is not the same. For these reasons only one type of oil, namely, cottonseed, was studied. [As is well known, the course of oxidation is affected by accelerants making it necessary to make definite control of these items, i.e., heat, light, moisture, certain metals.]

It is apparent that the peroxide test is far from being an ideal test for the measurement of rancidity. However, as it appears to be the best one yet devised, it was used in our work as a basic measure of oxidation, supplementing it with the occasional use of the other tests mentioned.

Before attempting to compare the various adsorbents on the rate of oxidation, it was decided to take a bleached oil and run it through a complete induction period and to compare our results with those in the literature.

Figure 2 illustrates the course of oxidation of our work as measured by color and peroxide value compared with those of Wheeler (Figure 1).[6]

In our search through the literature we did not find any great certainty as to the exact course of the oxidation of the molecule, particularly through the early stages. We believe that an examination of the curve brings out certain significant features.

Let us consider briefly the theory of what happens when an oil be-

Figure 1
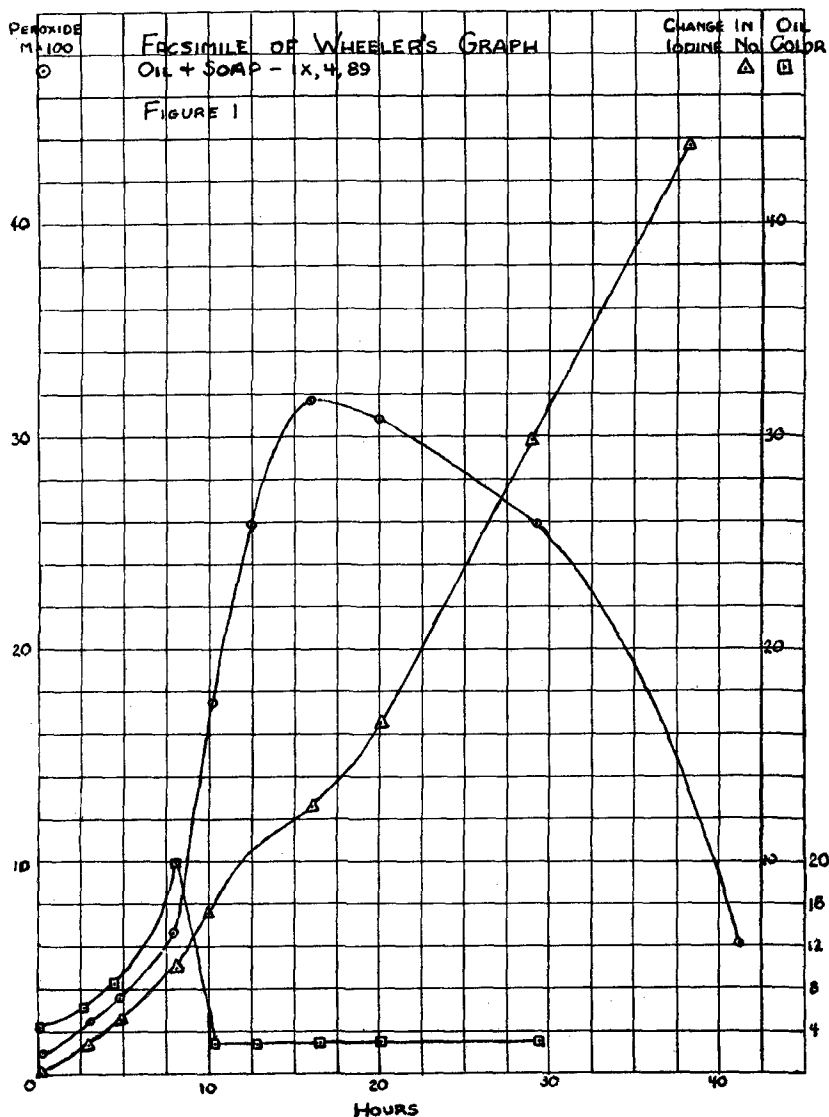
comes rancid. First of all, oxygen is adding to the double bonds of the oil and also to the double bonds of the color bodies. The potential of unsaturation apparently being much greater in the color bodies, oxidation occurs more swiftly here than in the oil itself. As these color bodies become oxidized, the color darkens, then suddenly lightens, indicating that the double bonds have become relatively saturated with oxygen which finally destroys the pigment structure. An interesting observation is that during the color reversion of cottonseed oil, it seems to be only the red color that is affected. No conclusion has been drawn from this.

The first rise of the peroxide curve to point A is concave to the time axis which is what we would expect with a regular mass action where the reaction becomes progressively slower as the reactants become used up (Figure 2).

Figure 2
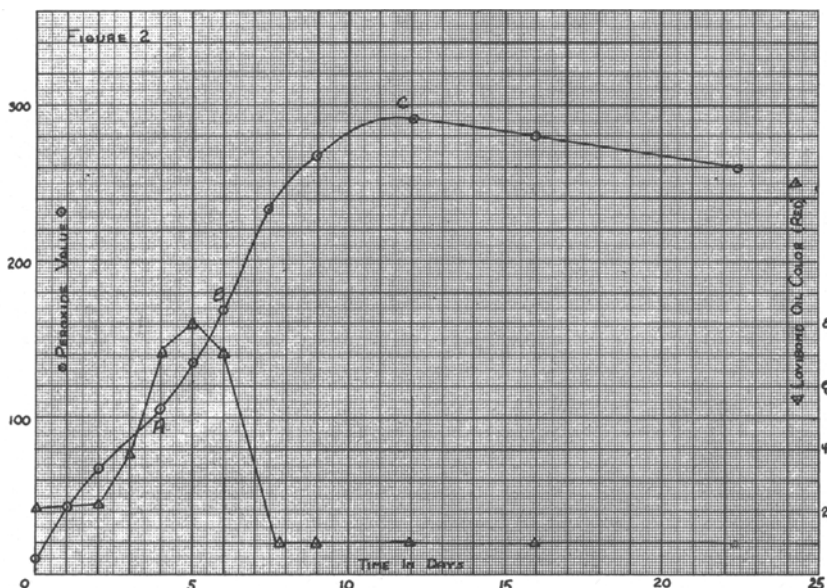
At the point A up to B this curve is convex to the time axis and this is also characteristic of the color reversion curve in the majority of our later comparisons. The physical significance of this would ordinarily be interpreted that the reaction is here proceeding at an accelerated rate proportional to the new products being formed.

The thought that it might be a condition due to auto-catalysis occurred and we carried out the following experiment with this in mind. The following samples were placed in the incubator:

1. Sample of fresh cottonseed oil,
2. Sample of partially oxidized cottonseed oil,

3. Mixture of 1 and 2 (ratio 4:1).

At regular intervals the samples were withdrawn and 1 and 2 were mixed in the same proportions used in the preparation of the original mixed sample. The results show no appreciable difference in the peroxide test (Table I). From this

it was concluded that the presence of an oxidized oil had not accelerated the rate of the oxidation of the fresh oil.

This indicated that autocatalysis was not taking place, at least within the range up to maximum peroxide value.

Probably the accelerated rise in this part of the curve may be explained by the depletion of the antioxidant color bodies which is occuring in this region. [From the organoleptic standpoint, Wheeler[6] observed that the flavor of the oil became "off" at a point just after

the decomposition of the color bodies.]

Present data is really insufficient on which to satisfactorily interpret the curve beyond the point B. General considerations by Hamilton and Matill[11] lead us to believe that the earlier oxidation products termed moloxides are measured by the

TABLE I
First Run

	Peroxide Value 1st day	Peroxide Value 2nd day
Mixed before incubation	55.3	76.2
Mixed after incubation	55.0	77.2

Second Run

	Peroxide Value 1st day	Peroxide Value 2nd day	Peroxide Value 3rd day
Mixed before incubation	59.8	77.0	101.5
Mixed after incubation	59.7	78.9	103.2

peroxide test. These are then further oxidized to more stable products which are not measured in the test.

So it will be apparent that beginning at some point (probably B) the curve represents a net result. New moloxides continue to form giving a further upward trend, and against this occurs the conversion of moloxides to stable oxidation products tending to bring the slope down. At the point C this latter effect has over-balanced the former and the curve reverses and shows descending slope.

At a point following the peak of the peroxide curve, it was noticed that the resulting oil was very viscous suggesting the possibility of polymerization or condensation, as well as decomposition. The concept of condensation may be further strengthened by Andrew's[12] observation that during the decomposition of a rancid oil hydrogen was evolved in greater volume than any other gas.

The work from here on was conducted according to the following scheme: To compare the induction periods of various commercial activated carbons, then of various commercial activated earths, and finally of mixtures simulating actual plant practice.

Inasmuch as the oil has definitely lost its salability after the point of color reversion, it was decided that in comparing the induction periods of various adsorbents it was

TABLE II
Original Refined B. P. S. Y. Cottonseed Oil
Peroxide Value—10.0

Adsorbent Used	Concentration of Adsorbent	Peroxide Value	Kreis
Activated Clay A	1%	1.5	Sl. +
Activated Clay B	1%	3.5	Sl. +
Activated Clay C	1%	3.8	Sl. +
Activated Carbon A	1%	11.7	Neg.
Activated Carbon B	1%	15.7	Neg.
Heated Blank	0%	21.0	Sl. +

only necessary to carry them through this point.

The first runs gave us definite indications of the difference between adsorbents. Our work showed little parallel between the Kreis Test and the peroxide value, at least where low concentrations of peroxides were found (Table II). It will be noted that the sample bleached with activated earth gave an initial peroxide value of 1.5, but showed a slight Kreis Test. On the other hand, the carbon treated sample having a peroxide value of 15.7 gave a negative Kreis Test. It was worth noting that in either case this initial removal did not definitely indicate the course of the subsequent induction period, although frequently the greatest removal showed the poorest stability. Heating the refined oil without any adsorbent under the conditions of running an A.O.C.S. bleaching test, raised the peroxide value from 10 to 21 as shown in the table. The peroxide values of the bleached oils ranged from 1.5 to 15.7, indicating that in all cases the adsorbent removed some of the peroxide bodies.

Of the commercial adsorbents—activated clays gave greatest initial peroxide removal. They also had the lowest pH (Table III). This suggested that a parallel possibly existed between pH and this initial peroxide removal. This was checked using an oil with a very much higher peroxide value (72.7) and bleaching with laboratory acidified
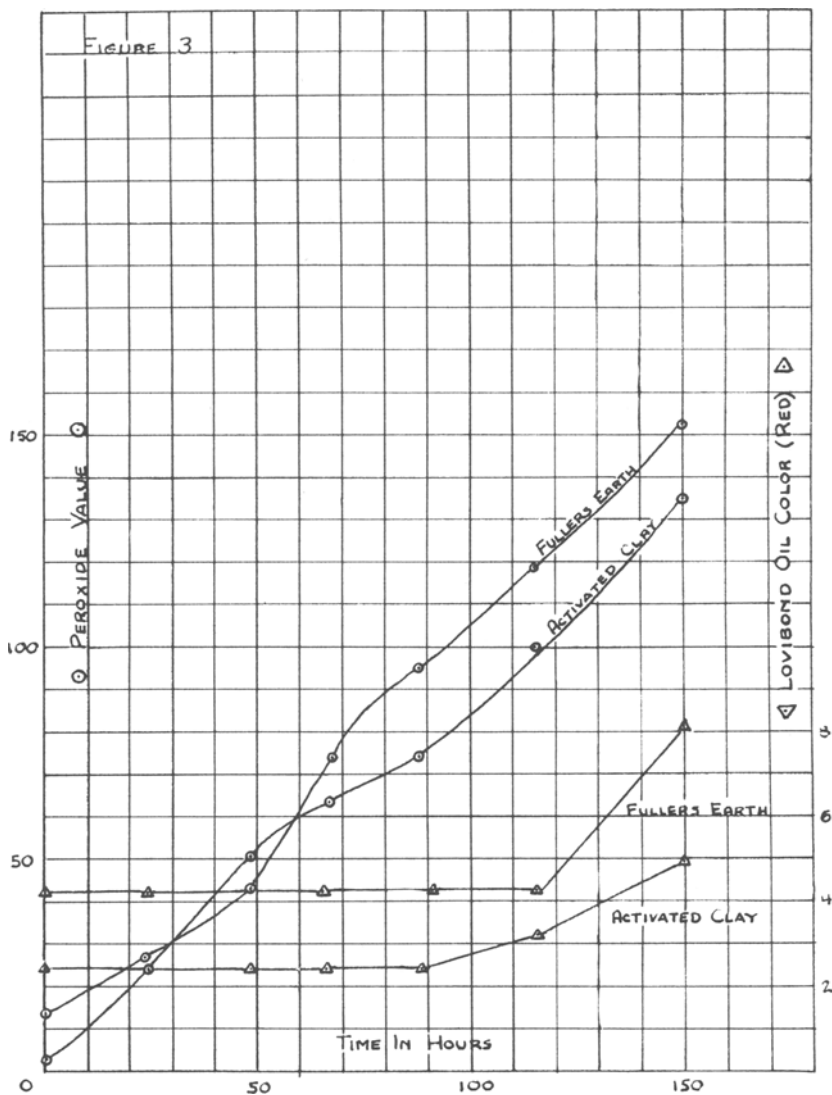

Figure 3.

carbons of low pH (Table IV). In one instance 6% of a carbon with a pH of 3.5 lowered the peroxide value from 72.7 to 3.8. This carbon was as effective as any of the activated earths in the removal of peroxide bodies. However, it is difficult at this time to appraise the value of this reduction from other than an academic viewpoint, as other work would have to be done to determine the stability and salability of this oil.

B. H. Thurman[13] found that lowering the pH of a clay increased its bleaching power. Our work confirmed this within certain limits. We investigated whether this might hold also for activated carbons in view of the effect of low pH in the case of both carbons and clays on peroxide removal. We were unable to improve the bleaching power of carbon by lowering the pH (Table V). The most effective pH range for carbons for color removal seemed above 6; on the other hand,

TABLE III
Bleached Oxidized Cottonseed Oil
Peroxide Value—43.5

Adsorbent	Concentration of Adsorbent	pH of Carbon	Peroxide Value
Clay A	6%	7.4	50.1
Clay B	6%	7.0	37.0
Carbon A	6%	6.3	34.9
Carbon B	6%	5.9	30.0
Clay C	6%	4.3	4.1
Clay D	6%	4.1	2.5
Heated Blank	0%	...	62.6

TABLE IV
Bleached Oxidized Cottonseed Oil
Peroxide Value—72.7

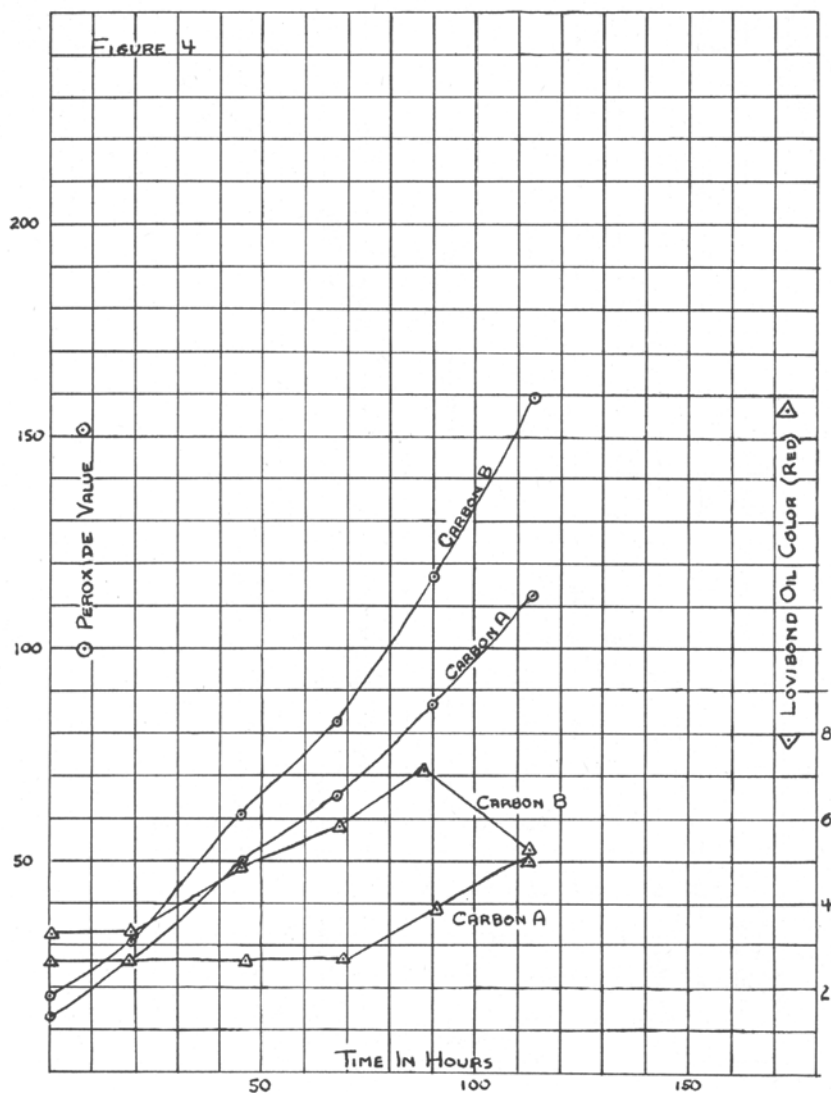| Adsorbent	Concentration	pH of Carbon	Peroxide Value
Carbon A (untreated)	6%	6.3	46.0
Carbon A (adjusted)	6%	6.0	32.0
Carbon A (adjusted)	6%	5.2	13.6
Carbon A (adjusted)	6%	4.2	11.6
Carbon A (adjusted)	6%	3.8	6.1

pH adjusted by washing with acid and drying.

TABLE V
Refined B. P. S. Y. Cottonseed Oil
Color—65 Y., 6.1 R.
Peroxide Value—11.9

Adsorbent	Concentration	pH of Carbon	Color Y.	Color R.	Peroxide Value
Carbon A	2%	6.3	20	2.1	8.5
Carbon A (adjusted)	2%	5.3	20	2.1	6.0
Carbon A (adjusted)	2%	4.5	20	2.2	5.4
Carbon A (adjusted)	2%	3.9	20	2.4	2.7
Carbon A (adjusted)	2%	3.5	20	2.5	2.7
Heated Blank	0%	...	35	5.8	22.3

pH adjusted by washing with acid and drying.

Figure 4

activated clays seemed most effective with a pH ranging from 3.5 to 4.0. The fact that lowering the pH of activated carbon improved the peroxide removal but not the bleaching power is a striking example of selective adsorption.

It appears, as would be expected, that within limits greater concentration of any adsorbent gives greater bleach and initial peroxide removal. While as previously mentioned, a low initial peroxide value is frequently followed by a comparatively poor induction period, this does not necessarily result. In fact, the use of a bleaching adsorbent does not need impair stability. This subsequent stability is influenced by the amount and particularly the type of adsorbent used.

The next work involved comparing the induction periods of oils bleached with a number of various adsorbents within each class. The results showed that there are definite differences between the adsorbents within any one of the classes.

Space does not permit the illustration of all our results at this time, so we have used selected graphs of different types. Figure 3 shows a graphical comparison of a satisfactory activated clay against Standard Fuller's Earth. It should be noted that Official Fuller's Earth was not the worst clay tested but was chosen as it may be quoted as a standard. Figure 4 shows the same comparison between the most and least satisfactory activated carbon.

Inasmuch as pigments are considered to have anti-oxidant power, it might be thought that an adsorbent that is most effective in removing color should also produce the least stable oil. This was usually found to be true but the results were not entirely consistent. The curves show that there is no definite relation between the peroxide and color curves. They further il-

lustrated that all activated earths do not act in the same manner on an oil. The same is true of activated carbons. As a matter of fact, in the case of activated carbons the one that bleached the best and removed the greatest amount of initial peroxides (Figure 4) gave much better stability to color and peroxide formation.

To round out this work, cottonseed oil was treated with (1) Standard Fuller's Earth, (2) fuller's earth-carbon mixture, (3) activated earth, (4) activated earth-carbon mixture. The concentration was so regulated as to give a bleached color of 20 yellow and 2.0 red, and the proportionate carbon to clay was so adjusted as to simulate plant practice. In the selection of carbon and activated earth, choice was made of those which gave the best results in the work just quoted. In view of the superiority of the carbon selected when used alone, it was expected that it would when mixed with Standard Fuller's Earth or activated earth, produce an improvement in the stability of the bleached product. Figure 5 shows that this is true. Employing equivalent total concentrations, the carbon-fuller's earth mixture gave us better bleach, better peroxide removal and much greater stability of color and peroxide formation. The same proved true in the case of the activated clay-carbon mixture in all respects.

Summary

The results when graphed produce curves that correspond closely in type to those found in the literature.

While the course of oxidation reaction during the induction period proceeds with an accelerated rate during the early stages, it does not appear to be due to the formation of positive catalytic bodies. We believe that it is due rather to the depletion of stabilizing bodies.

Bleached oils of certain type, i.e., cottonseed, are not necessarily more unstable than unbleached oils, the factor depending on the selection of the proper adsorbent.

Lowering the pH of an adsorbent gives lower initial peroxide value. However, this does not of itself improve the subsequent stability. In fact, a greater initial peroxide removal was frequently followed by subsequent instability.

In their effect on stability variations were found between the different classes of adsorbents, and

differences within each class. It is not known why this is so.

The absence of any relationship between the various tests applied to oil immediately after bleaching is evidence of selective adsorption. It might be possible to deduce from this that the adsorbents which give poor induction periods are selectively adsorbing stabilizing bodies that are not measured by any of the existing tests.

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Figure 5
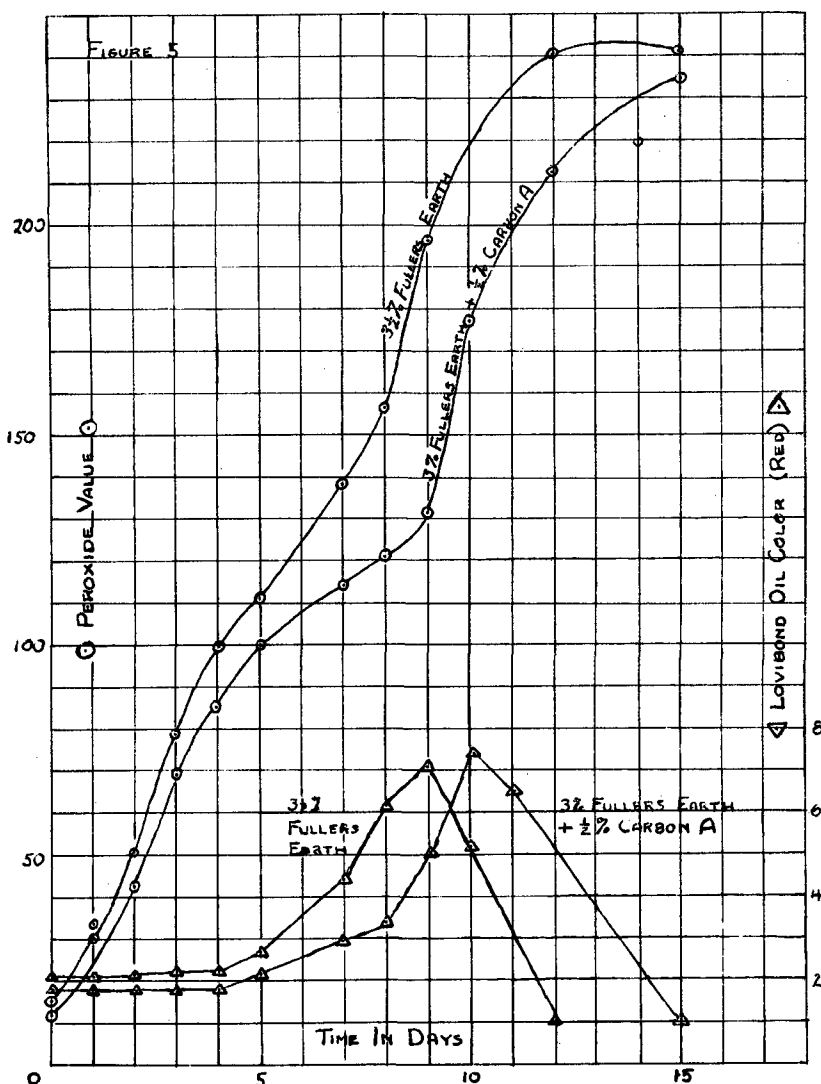
A NEW NON-CRYSTALLIZING GUM ROSIN

By S. PALKIN, Senior Chemist, and W. C. SMITH, Associate Chemist

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ROSIN is virtually the only form in which the solid or non-volatile part of pine oleoresin finds its way into commerce. Its vitreous or non-crystalline character is so commonplace as to be taken for granted, and the fact that a substantial proportion of rosin consists of crystallizable acids is almost overlooked. The formation now and then of clusters of crystals within the solid rosin, and for no clearly accountable reason, brings the buyers and sellers of rosin to the realization of this crystallizing tendency and the complications which this slight variation in form entails.

As is well known, the presence of appreciable crystallized material in rosin constitutes a serious objection to its use in various industries, particularly in soap and paper-size-making, where the crystallized rosin, because of its high melting point, enters into reaction with alkali and other materials much more slowly than the uncrystallized, and tends to granulate instead of becoming the smooth, soapy emulsion desired in soap making. Moreover, mere tendency to crystallize, even though crystals have not actually appeared in the original rosin, will bring about crystallization in rosin preparations such as, for example, core oils and

adhesives, comprising generally solutions of rosin in linseed oil or petroleum and lubricating oils, thus seriously interfering with their use.

Why some rosins tend to crystallize and others do not, and what testing methods can be applied to rosins to determine the latent or potential crystallizing tendency before any crystallization has taken place are matters now being studied by the Naval Stores Research Division, and a report of this investigation will be published in the near future.

The present paper deals with a rosin fraction, obtainable exclusively from pine gum, which has shown