ence in long spacings between Forms I and II appears to be outside the experimental error. In the case of Form I, the present data agree almost exactly with those of Clarkson and Malkin.

The technique employed in the present investigation apparently permits the observation of reflections not recorded by previous workers. The data of Clarkson and Malkin were obtained by an oscillating-sample method with pressed or melted layers which enhanced reflections for the long spacings. Control of the cooling rate was depended upon to produce the particular crystal form desired in the melted layers. It is noteworthy that in a later investigation of monoglycerides Malkin and el Shurbagy (7) concluded that the Clarkson-Malkin technique produced layers unfavorably oriented for the observation of side spacings and in subsequent work abandoned it in favor of a method which employed specimens solidified in the form of thin rods.

In the light of the present results it appears probable that both the "vitreous" and "*a*"-patterns of Clarkson and Malkin corresponded actually to Form III, and that differences between the two arose simply from conditions that were in one case favorable and in the other case unfavorable for the crystal orientation requisite for the observation of well-defined spacings.

As would be expected in a mixed material, the crystal spacings for the more complex Form I of the hydrogenated cottonseed oil did not conform to those of corresponding forms of either of the major components of the oil, namely tristearin and β-palmitodistearin. However, the pattern of the simpler Form IV was very similar to those of the pure components, although not in exact agreement with either.

Summary

1. Melting points and x-ray diffraction patterns have been determined for cottonseed oil hydrogenated to an iodine value of less than 1, and for a very pure sample of tristearin.

2. Contrary to the observations of previous investigators, the x-ray patterns indicate a well-defined crystal structure with a sharp long spacing and a single sharp short spacing in the lowest-melting form of tristearin. A new pattern, with two short spacings and a long spacing, was observed in tristearin of intermediate melting point.

3. Four polymorphic forms of the hydrogenated cottonseed oil were detected. The x-ray pattern of the lowest-melting form of the hydrogenated oil was similar to that of the correspopnding form of tristearin. The pattern of the highest-melting form of the hydrogenated oil differed from that of either tristearin or β-palmitodistearin, the major components of the oil. Distinctive patterns for the intermediate forms of the hydrogenated oil could not be obtained, presumably because of the instability of the lower melting forms at room temperature.

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Evaluation of Color Quality of Crude Soybean Oil — Some Data and Difficulties Incident to Developing a Suitable Test for Off Grades[1]

An Elaboration of Some Aspects of the Bleach Test Committee Report and of Other Unpublished Recent Technical Committee Work

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IT SHOULD hardly be necessary to remind our oil chemists and technologists of the distressing consequences stemming from the occurrence of an early severe frost throughout most of the soybean-growing States in the Fall of 1942. Most of us lived with and struggled with those consequences during the succeeding twelve months, and many of us no doubt kept our fingers crossed during the frost-susceptible weeks in the Fall of 1943, while the new crop was maturing. In this there was added anxiety in the circumstance that heavy rains and floods in important sections of the most concentrated bean-growing areas had caused deferring of planting or replanting weeks beyond normal planting time.

This arresting of the maturation process in a very large proportion of the beans grown that year could hardly have occurred at a worse time from the standpoint of those in the industry — whether farmer, processor, or refiner. Consider these things: the crop had expanded to roughly double the previous record size, and the oil production was to go well over the billion-pound mark, exceeding cottonseed oil tonnage for the first time. We were at war and could ill afford to lose any degree of quality and especially any reduction in yield. Then, there emerged a realization in the trade of a need for revising trading rules for the settlement of crude soybean oil transactions, rules which

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[1] Paper presented at the Spring meeting of the A. O. C. S. at New Orleans, May, 1944. Opinions expressed in this paper do not necessarily represent those of the Bleach Test Committee.

must rest upon a technical and scientific basis—specifically, a measurement and evaluation of those properties of the oil which were most severely modified and distorted as a result of the frost damage and subsequent influences. Finally, consider the further complication incident to the impact of having Government corporation and price control offices participating in and regulating the industry and the oil trade.

All this added up to the creation under Government instruction of emergency Task Committees, to the meeting on short notice of Executive Committees, Rules Committees, and Technical Committees, and in circumstances when they could be convened, of A. O. C. S. Committees on Methods—as well as the appointment within all of these, of special subcommittees to achieve in the minimum of time the successful solution of some particularly urgent problems dealing with methods and the evaluation of quality on oils the like of which none of us had ever before seen.

It is the purpose of this paper, then, to report on the quality of the oils encountered at various times during the crop year, on the scientific problems they posed for the satisfactory evaluation of these qualities with the apparatus and methods available, and something of the way in which these problems were attacked and solved, or by which we expect to solve them. This is a report on the work of some of the committees and subcommittees mentioned; and in a sense it is a progress report, because as long as there exists the potentiality of having another season with a high incidence of damaged oil as in 1942-43, it is felt that the methods finally adopted be capable of accurately and reproduceably evaluating the qualities of the off-quality oils right down to what may be the designated "sample grades." The job is not yet finished, as I will show at the end of this paper, but we believe the end is in sight.

Early Green Oils—the First Problem

It seems appropriate to run through the crop year chronologically, noting the types and qualities of oils encountered, and briefly the measures taken to deal with these in trading. Table I shows the crude, refined, and bleached colors, as well as heat-bleach colors on a variety of oils of graded chlorophyll content, as encountered up to early December, 1943, with two substantially normal 1941-42 oils for comparison. Three different bleaching clays were used, and the bleached oil from each of these was further bleached at deodorization temperature under inert atmosphere.

For the purpose of this study, and particularly to get a single quantity which could be plotted graphically, the yellow and red values are combined in an arbitrary way to give a measure of "total absorption"; and to make this quantity more representative, the rough quantitative measure of a third factor is included. This is "% neutral absorption" as determined by the number of excess color glasses used in obtaining the match, (bearing in mind that the A. O. C. S. method assumes that a substantially correct brightness match occurs with the use of two or three color glasses). This takes account of the loss of light by reflection from the two surfaces of each color glass, assumed to be 9% of the light incident to the first surface.

Figure 1 shows the variation of most of the different color properties listed in Table I, plotted against one of them selected arbitrarily as the independent variable. It is clear that the refined oil color and the A. O. C. S. official bleach color both correlate well with the crude color, and it is equally clear that even one of the moderately-active natural commercial bleaching clays (East Texas clay) removes most of the excess color in the worst oil shown here, whereas a moderate percentage of a highly active acid-treated clay and a little carbon removes substantially all of

TABLE I

Old Crop Oil						New Crop Oil (1942-1943)			
	Designation	Normal Iowan D4	Mixed Origin	Upstate Illinois	2 pts. Illinois 1 pts. Iowan	Iowan D2	2 pts. Iowan 1 pts Ill.	Iowan D	Iowan Composite D3
A	Crude, 1″ y, r, & N Total [1]	60Y 7.5R T 135	60-6.5 125	150Y 5.6r 20N 226		153Y 6.1r 1.0 bl 27N 263	too dark	240Y 8.6 + ?N 326 + [3]	too dark
B	Crude, ½″	35Y 4.5r 80	35-3.5 70	90Y 2.5r 9N 124		90Y 2.1r 27N 138			115Y 3.7r 46N T 198
C	Refined, 5½″	70Y 9.0r T 160	60-8.8 148	220Y 14 0R 80N 440		Colors much too dark for satisfactory reading			
R	Refined, 1″ (= R)		35-3.4-40N 29	55-1.7 72	115-2.1 136	120Y 1.8r 138	150-2.2 172		120Y 2 4r 34N T 178
S	Bleached, Official (= S)	50-3.1 T 81	45-3.6 81	55-3.5 90	140Y 3.6r 19N 195	90Y 2.3r 27N 140	160Y 3.8r 19N 217	105Y 2 8r 1.0 bl 55N 208	125Y 4.2r 61N T 228
X	Bleached, 6% X Earth (= X)	35-2.1 T 56		35-2.5 60		45Y 2.1 66			45Y 3.2r 77
F	Bleached, 2%F, 0.1% C (= F)		25-2.9 54	20-2.1 41	25-2.4 49	35Y 2.2r 57	35-2.5 60	[4] 17-1.4 31	
RH	R Oil, Heat Bleached [2]		20-0.8 28	Too dark to read					
SH	S Oil, Heat Bleached [2]		6-0.8 14	15Y 0.5r 0.4 bl 28	45Y 0.7r 80N 139, v. dull	25Y 0.3r 0.5 bl 70N 108	80Y 0 3r 75N 161 v. dull		
FH	F Oil, Heat Bleached [2]		10-1.1? 21	6-0.7 13		7-0.5 12	8Y 0 8r 16		
XH	X Oil, Heat Bleached [2]			11Y 0.5R 16		11Y 0.4r 15N 30			18Y 0.6r 5N 29

[1] Total = Y + 10r + 20 bl + % Neutral absorption + 20 Bl + N.
[2] 3 to 4 hrs. @ 410° to 430° F. under hydrocarbon atmosphere.
[3] Rough estimate; oil very dull.
[4] 3% "F" earth, 0.2% carbon.

Brightness Equivalence or Interchangeability of *Yellow* and *Neutral* Values in Dark Green Oils

Oil No. 1	Oil No. 2
H. S. 145y/3.2r; Equiv. total, 177	150y/2.1r — 19N; Equiv. total, 152
E. F. & H. S. 115y/3.2 + 27 Neutral; Equiv. total, 174	100y/2.3r + 27N; Equiv. total, 150

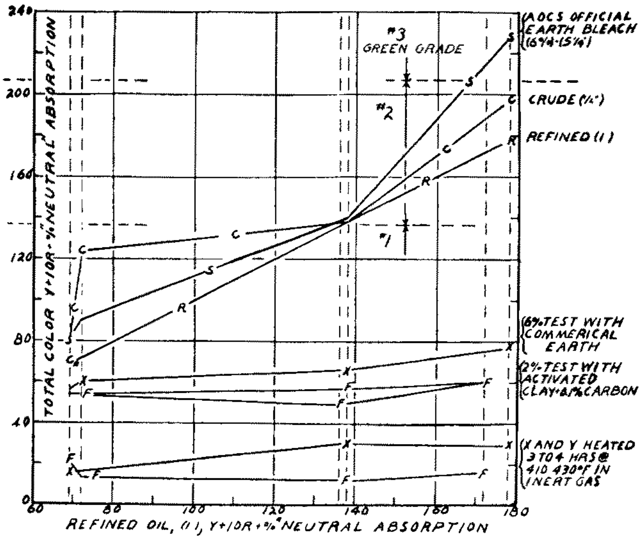

FIG. 1. Graph showing correlation of "greenness" in frost-damaged crude, refined, and 6% A. O. C. S. refined bleached soybean oils—also substantially complete removal of the green by use of suitably active bleaching materials, especially with subsequent heat treatment simulating deodorization. Distance along both axes indicates degree of frost damage. Points at extreme left represent a normal, undamaged oil. These were all early season oils.

the excess color; and after heat-bleaching at deodorizing temperature in the latter case, the difference between the normal crop oils and the worst green oils shown has practically vanished.

It is to be noted that later in the season some types of green oil showed less satisfactory bleaching response, some giving rise to an abnormal, brilliant clear green color during hydrogenation. Nevertheless, this graph shows why refiners had little difficulty processing the green oils encountered in the first part of the oil crop year. During that period oils darker than the darkest indicated here were rare, i.e., No. 3 green grade oils.

Methods in Green Grading

IT MIGHT be mentioned here that had the yellow color reading only been taken as the primary variable and measure of chlorophyll in the oil, the general properties of the graph in Figure 1 would not be essentially different. Hence, in the absence of the general availability of other apparatus, such as spectrophotometers, the earliest method used to measure and designate grades, as determined by excess green color, was the amount of yellow required to give the best match, with a fixed red. Thus, an emergency tentative trading rule was established on this basis and was actually used for a few weeks while a subcommittee developed a more satisfactory method.

This subcommittee was headed by our Society's recently retired President, Dr. Lamar Kishlar, who with his assistant, Mr. Harold Ory, submitted to the N. S. P. A. Technical Committee within a matter of weeks an ingenious and simple filter photometer method of grading colors on these dark green oils, one which required practically no additional apparatus and which could be used by a grammar school-trained laboratory technician. After the method had been critically examined and tried by the members of the Technical Committee, it was submitted to the trade for use in grading the green crude soy oil—specifically, as prime, No. 2 green grade, and No. 3 green grade. Figure 2 is a reproduction of soy oil spectrophotometric curves and curves on the optical elements used in the method, and I am quoting below an explanation as supplied by the originators of the method in the Ralston Purina laboratories:

"The accompanying plot of spectral transmission curves for a series of soybean oils shows that the oils all had the common characteristic of transmission minimum in the region of 675 mμ, commonly attributed to the presence of chlorophylls. The value of the transmission minimum appears to be a good index of the quality of the oil both as to green color resulting from red absorption and to other absorbing materials present which have some absorption at 675 mμ, but not the pronounced effect of chlorophyll.

"If the visual wavelengths beyond 640 mμ are isolated by means of a filter (Corning No. 2403) as shown on the plot, the average transmission in this range as integrated by the eye will be an index to the quality of an oil sample. The character of the portion of the oil curve so isolated is approximately equivalent in visual color to that which would be obtained by uniformly cutting out a given percentage of all wave lengths in the desired region. This could be accomplished by a neutral density filter of known transmission.

"Hydrated nickel sulfate in solution possesses a transmission curve such as shown in the plot. In the region beyond 640 mμ the transmission is essentially the same for all wave lengths and will thus give the effect of a neutral density filter for this range.

"Thus, if the nickel sulphate solution and an oil are matched after cutting off all wave lengths below 640 mμ by means of a filter, no differences in color are present to disturb matching. Comparison can then be made solely on the basis of total light transmitted without the difficulties due to visible color differences."

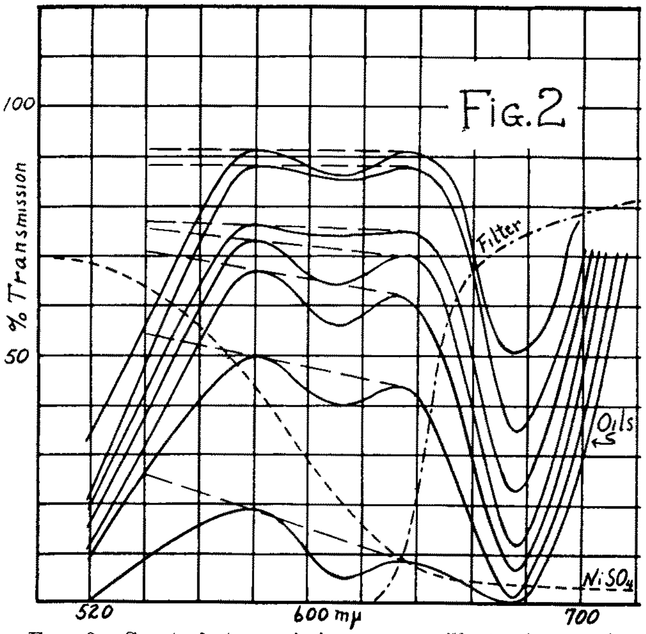

FIG. 2. Spectral transmission curves illustrating various amounts of green in crude soybean oil due to chlorophyll associated with early frost damage of the soybean crop. These curves, together with those representing the spectral transmission of the Corning Pyrometer Red Filter No. 2403, and of a solution of nickel sulphate, constitute the basis of the filter-photometer method of green crude soy oil grading originated in the laboratories of the Ralston Purina Company.

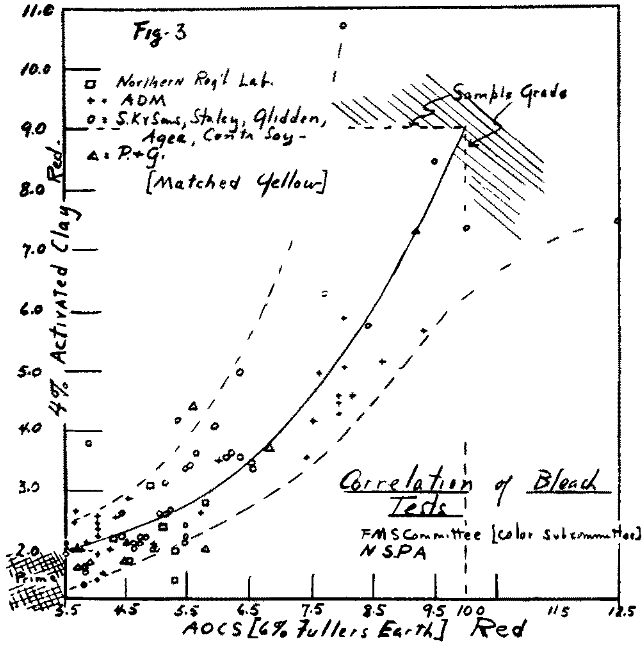

FIG. 3. Relation of refined bleached color on crude soy oils by two different bleach tests. A large proportion of these were frost-damaged oils; some were field damaged.

In less scientific language this simply means that viewed in a monochromatic light, everything appears to have the same color, i.e., the oil being evaluated, and whatever may be used to match it against, whether that may be a variable density neutral wedge, or the varying depth of some colored chemical solution, or different concentrations of some colored chemical solution, as was adopted, in this instance. The only differences apparent therefore are in brightness, and it is only necessary to decide whether the oil is equal to, lighter than, or darker than the standard solution. According to the writer's experience and that of others with whom he has discussed this, the use of this method has been entirely satisfactory in trading.

Winter Weather Damage

ALONG in February, and especially in March '43, there began to arrive at some of the mills large quantities of soybeans which had remained unharvested in the fields during the winter, which abuse had damaged them in a way to render the refined oil highly resistant to ordinary bleaching methods. Furthermore, this type of oil did not process into satisfactory finished edible goods; or, if it might be deodorized into an apparently acceptable product, this showed a strong abnormal tendency toward color and flavor reversion. Here, then, was obvious need of some other kind of test to evaluate the quality of such oils. Experiment and experience* showed that the quality of an edible oil correlated rather well with the indications of the official A. O. C. S. bleach test; and an industry Task Committee, formed at government behest, membership of which was equally divided between processors and refiners, recommended this test as the basis of color grading. Subsequently, after further study of the factors involved, the N. S. P. A. Technical Committee corroborated the Task Committee's recommendation, and the A.O.C.S. bleach test was well under way to becoming the basis of a new Trading Rule. Eventually, it was acted upon favorably.

Then, some mills began to receive beans from the worst frost areas which yielded some oil the like of which had not been encountered during the previous five months of crushing that season's beans. The A. O. C. S. refined bleached color was either so dark as to be entirely unreadable in most of our laboratories, or perhaps was readable with difficulty in a few laboratories which had enough high-denomination yellow glasses and had devised color glass adapters in which 12 to 18 color glasses could be piled together. Worse, even assuming that all laboratories could do this, the discount scale which had been set up on the basis of the A. O. C. S. refined bleached color gave ridiculous figures for this type of oil, altogether out of proportion to the oil's real value. In fact, while distinctly in the discount class, some refiners were using this oil without too much trouble, and this experience plus some controlled laboratory runs covering all stages of processing, showed conclusively that the A. O. C. S. bleach test failed to grade this kind of oil fairly. Thus was another subcommittee born!

After making many determinations of color, using the nickel sulphate-red filter photometric method, with promising but not entirely satisfactory results, the committee was forced with some reluctance to turn to the use of an acid-activated bleaching clay as a potential standard test bleaching clay, as the oil responded fairly well to such a clay from the test standpoint—especially it removed the excess green; and indeed it seemed that the use of such activated clay in plant practice was the basis of successful utilization of this extremely dark green crude soy oil, which A. O. C. S. official earth hardly touched.

A few bags of a certain lot of clay were thus laid aside and designated "primary standard," and distributed to the committee members and others; then several series of bleaches at different percentages on various types of off-quality soy oils, winter-weather damaged as well as frost-damaged and normal, led to the adoption of 4% as the percentage for a standard test. Next we set out to accumulate a quantity of data comparing this 4% activated clay test against the A. O. C. S. bleach test. About two hundred comparisons were made in at least eight different processor-and-refiner laboratories and in one commercial laboratory. A plot of a representative group of these comparisons is shown in Figure 3. The moderate scatter of the points is a result of the variable character of the oils, specifically differences in the pigments resulting from different causes of the off-color condition, and differential response of these pigments to the two clays. Also, adding chlorophyll to an oil actually reduces the red reading, as will be shown presently. Hence, in comparing the bleaches on oils containing varying amounts of chlorophyll, or no chlorophyll, using two bleaching clays, one of which has a high absorptive capacity for chlorophyll, the other a very low capacity, we are sure to get a correlation of the two tests which leaves something to be desired in preciseness. Certainly, there is no reason to expect equivalent responses to the two different bleaching clays of oils rendered off-color by winter-weather damage on the one hand, or bin-burning on the other, or setting

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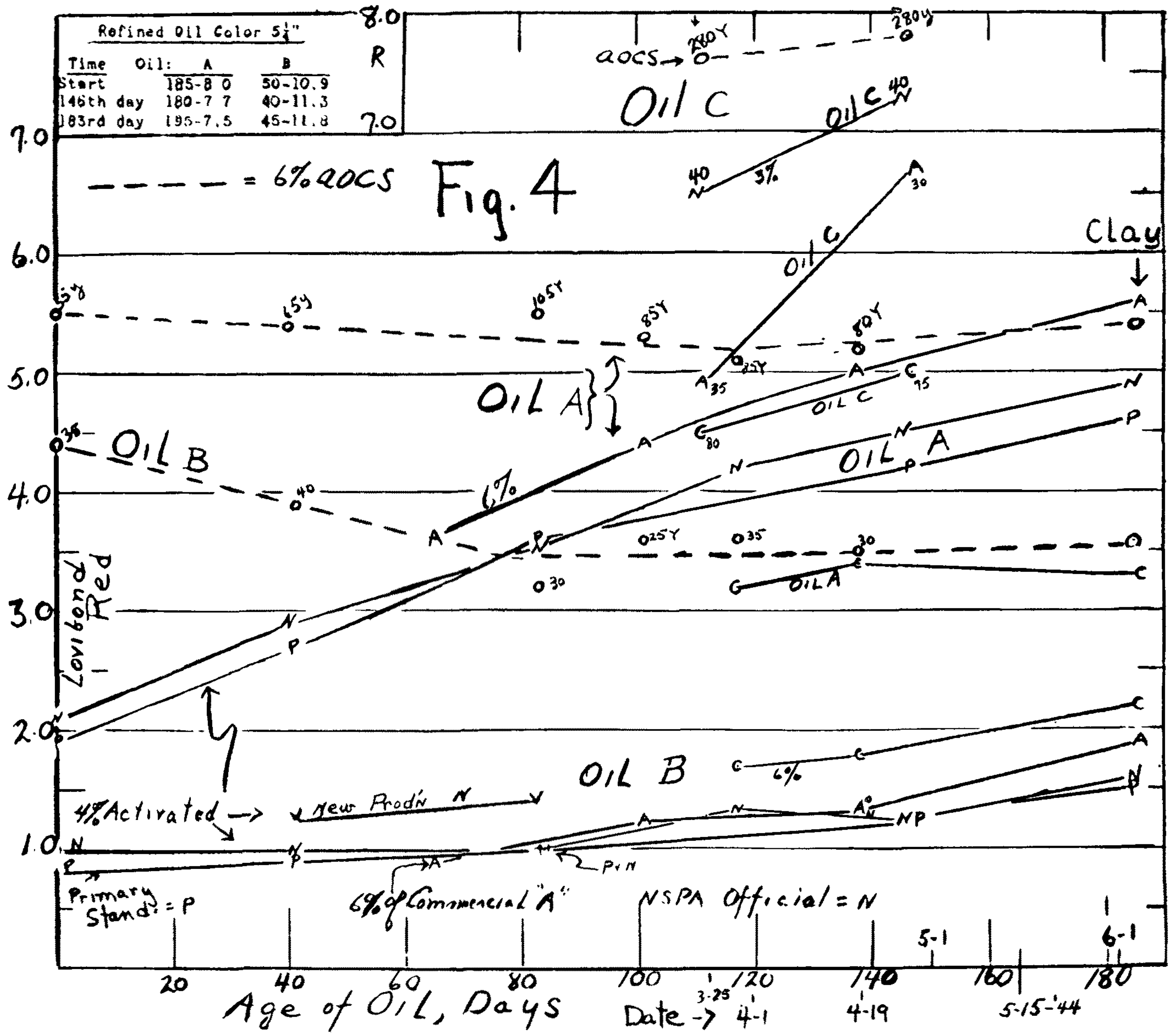
* A paper reviewing one company's experience in connection with this principle was presented at the 1943 Spring meeting by Mr. J. H Sanders of the Procter & Gamble Company, under the title, "Predicting Flavor Stability of Soybean Oil." [Oil and Soap *21*, 357 (1944).]



Time	Oil: A	B
Start	185-8 0	50-10.9
146th day	180-7 7	40-11.3
183rd day	195-7.5	45-11.8

Refined Oil Color 5¼"

FIG. 4. Deterioration in Bleaching Response of Three Refined Soy Oils Against Various Bleaching Clays.

Key:

Oils

Oil A; 1942-3 Crop; slightly frost-damaged oil.
Oil B—1943-4 Crop; normal quality.
Oil C—1942-3 Crop; strongly frost-damaged (see Table 4 and Fig. 7).

Clays

N, P, V—Activated clay 4% bleach.
C—Commercial natural clay 6%.
A—Commercial natural clay 6%.
O—Official A. O. C. S. Earth.

Figures by the plotted points in certain cases represent the yellow color readings.

of the color by improper conditions employed in processing in a third instance. In fact, on this graph one of the points deviating most widely from the group in the higher color range represents an oil which was obviously contaminated with lubricating oil, as evidenced by strong typical mineral oil fluorescence. This happened to be one which favored the A. O. C. S. official Fuller's earth. Still another factor contributing somewhat to the scatter of these points is one associated with discrepancies in color readings as between different laboratories, resulting partly from different ideas as to what constitutes a color reading on certain abnormal types, but mostly from imperfections in our official method for reading Lovibond colors, especially when applied to certain abnormal type of soybean oil. Finally, the idea of a correlation of the indication of two different tests loses all meaning in instances when one of the tests does not yield an oil on which the color can be read at all, i.e., by the method designated.

In a sense it was fortunate that this work had to be done during a season when there was such a variety of off-color oils, since the translation of indications from one bleach test to another would be on the basis of the average of several different sources of off-color. Conceivably, we may have a season when the oil is predominantly frost damaged while winter-weather damage is entirely lacking; or there may be weather damage and no frost damage, although in 1942-43 the winter-weather damage was an unfortunate consequence of a combination of conditions incident to wartimes—mainly, a record crop and a farm labor shortage at the same time; and this combination may never again occur.

At any rate, a Trading Rule was formulated around the use of 4% activated bleaching clay, which we felt confident would grade any type of soy oil likely ever to be encountered; but it is obvious from the above that it would not always grade all oils in the same order in which the A. O. C. S. official bleach test might grade them.

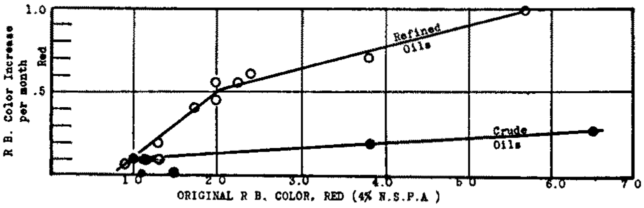
As to which grading might most truly represent the quality of the oil with respect to commercial value, it is believed that the activated bleach does so for several reasons: (1) the 6% of A. O. C. S. earth fails to remove all of the chlorophylls responsible for the green color, presence of which depresses the red reading, as will be shown; (2) the A. O. C. S. Official Fuller's Earth may practically be considered obsolete from the standpoint of commercial practice, while (3) activated clays are being used more and more in the commercial bleaching of edible oils.

Stability of Test Clay

THROUGHOUT the course of the preliminary work consideration was given to the question of possible deterioration of the activated clay on aging, and an effort was made to learn what was known about this factor, only to discover that existing information was either vague or entirely incorrect. In view of the meager evidence available, however, it was decided to renew the supply of official activated clay every six months, unless at the end of the first six months it may have been proved to be stable. Also, it was decided to establish the facts on this point as quickly as the nature of the problem would permit —which unfortunately could not be quick enough to settle this question before the launching of the new Trading Rule.

Our Society's Bleach Test Committee undertook the job of demonstrating either that the activated clay selected was sufficiently stable in activity to justify its use as a standard test clay, or of determining the rate of deterioration, should it appear not to be stable. The job was given to a subcommittee headed by Mr. J. H. Sanders of the Procter & Gamble Company.

The reports of the subcommittee and of the main Bleach Test Committee, and a supplement to these reports, abstract of which is published in this Journal, show that the problem was far from being as simple as it was first supposed, and there are still some questions to be answered. Briefly, the results have demonstrated that when soy oils are held in the refined state some change occurs in them which impairs the activity of activated and the more active natural clays, causing a deterioration of bleaching response on aging, this being quite noticeable even in holding a few weeks, in some cases. (See Figure 4.) While it was first thought that this change represented a deterioration in activity of the clays, a rather extensive study based on several different approaches finally proved conclusively that it was not the clays that changed; it was the oils. The rate of this deterioration is roughly proportionate to the original bleach color of the oil (Figure 5). Due most probably to its much lower activity (and hence less susceptibility to "poisoning"), the bleachability of the same oils does not deteriorate appreciably against A. O. C. S. Official Fuller's earth—in most cases not at all. Work on a limited number of oils, however, showed that when soy oils are aged as crudes, the deterioration of bleaching response (after refining) was much less, in fact only about one-fourth of the rate observed in the case of holding refined oils (Figure 5, Table II). However, more data are needed on this point, especially on extracted oils; and it is now being studied further.



COMPARATIVE DETERIORATION OF BLEACHING RESPONSE (4% ACTIVATED CLAY) ON SOY OIL—AGING AS *REFINED* OILS VS. AGING AS *CRUDE* OILS

FIG. 5. This shows that the poorer quality oils as determined by the refined bleached color, deteriorate more rapidly in bleach than the good, normal oils. When aged as crude, however, even the poorest oils show only slight deterioration. The two points to the right on the curve for crude oils represent oils C and D.

Also, there is not enough information on the behavior of refined soybean oil in bulk storage. In other words, does it show the same deterioration of bleaching response against activated clays that small lots

TABLE II

Change of Original Color and of Bleaching Response on Two Damaged Crude Soy Oils When Stored as Refined Oils and as Crudes

	Oil C					Oil D				
	Original		After Aging N Days		N Days	Original		After Aging N Days		N Days
	y	r	y	r		y	r	y	r	
Crude Color 1"	200	7.5	195	6.5	60	140	9.9	110	8.9	60
Refined Oil Color*	175	3.9	175	3.5	60	265	14.1	265	13.5	60
Aged as Refined Oils										
6% Clay C	80	4.5	75	5.0	36					
6% Clay A	35	4.9	30	6.7	36	35	8.0	35	8.7	25
3% Activated N	40	6.5	40	7.3	35					
6% AOCS Official	280	7.6	280	7.8	35	245	11.0	235	11.3	22
18% AOCS Official						90	5.1	85	4.9	50
Aged as Crude Oils										
3% Activated N	40	6.5	35	6.9	58					
4% Activated N	35	3.8	30	4.2	57	40	6.5	35	7.0	57
6% AOCS Official						245	11.0	240	11.3	58
18% AOCS Official	45	3.7	40	3.7	57	90	5 1	70	4.9	57

* 1" on Oil C; 5¼" on Oil D.

No change in FFA from original value of 1.2 on the crude.

Note that the change in bleach color on the aging *refined* oils was fairly pronounced in the case of both oils for the 22-36 days' holding period indicated—except against A. O. C. S. earth; even in this case on holding refined Oil D for 50 days. But note, too, that in holding the *crude* oils about two months the refined bleach color against the activated clay increased much less on both oils; and against A. O. C. S. earth, again, there was no significant change.

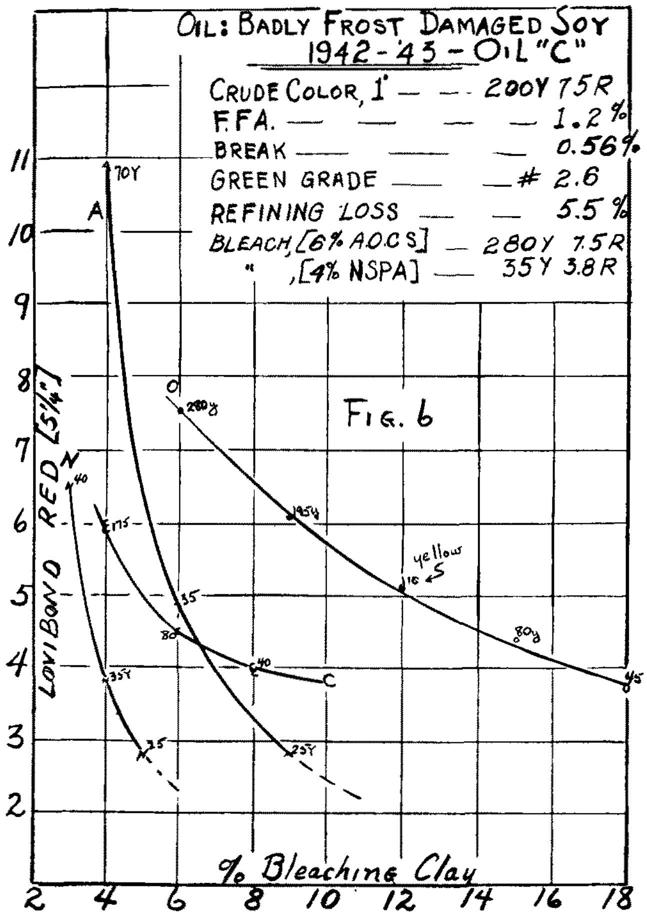


FIG. 6. Bleaching Response of Frost-damaged Soybean Oil Against Four Different Clays.

The depressing effect of chlorophyll on the red reading is shown by the relative flatness of the A. O. C. S. earth curve in comparison with the others. However, plotting the red reading alone gives a misleading idea of a clay's activity. For example, the curve for earth C crosses that for earth A for the same reason. The yellow readings opposite the different points show there was still considerable chlorophyll left in the oil in the case of the low percentages of clay C. When yellow color removal and the removal of "composite color," .1y+r/2, are plotted for this oil, as has been done in Figure 7 for oil D, a similar arrangement of the curves obtains, as in 7.

of refined oil (up to half a drum) exhibit? Although we would like to have an answer to this question, it will not be easy to obtain since apparently refined soybean oil is not stored in bulk to an appreciable extent. If refined soy oil in storage tanks deteriorates in bleaching response at about the same rate as in the case of samples, then we could consider that the bleach indications of these samples would truly evaluate the behavior of the oil. If, however, stored refined oil does not exhibit this rapid deterioration (and this seems more probable), then the use of an activated clay as a standard test basis would be very ill advised where the grading of refined oils is concerned. It would be necessary to designate that the bleach test be made within narrow time limits after drawing the sample, certainly within a week at most. Results between different laboratories would be comparable only if the tests were run at approximately the same time. Rechecks on the same sample could not be expected to agree with bleach tests made previously. To obtain a recheck after more than about a week, it would be necessary to resample the lot of oil represented.

These objections, however, do not apply to A. O. C. S. Official earth now designated for soybean oil; and since for trading purposes it would only be necessary to indicate whether refined oil is "bleachable" or not (rather than to grade it along an extensive bleachability scale, as in the case of crude soy oil), it is apparent that the present tentative A. O. C. S bleach test for soybean oil is the logical choice for designating as the basis of any trading rule which might ever be drafted *dealing specifically with refined oil.*

On the other hand, the data available at this time show that the deterioration of bleaching response occurring when the oil is stored as *crude* is only slight and is negligible in the case of normal quality oils; hence for the purpose of grading crude oils only, the activated clay can be considered quite satisfactory in a test for evaluating its refined bleached color—provided work now in progress confirms the earlier rather limited data.*

Natural Clays and Typical Off Oils

When it was thought in March of this year (1944) that some other clay, probably a natural one, would have to be found to serve as a standard bleaching clay, and especially after more evidence had accumulated to show that the type and quality of oil on which a given clay may be tested may determine to a large extent the relative response between clay and oil—and with the knowledge that supplies of the old 1942-43 crop were disappearing, even small quantities for test purposes, the writer made an especial effort to obtain enough of some typical types of 1942-43 damaged crude against which to evaluate several active natural clays in comparison with the two test clays which we have been discussing, i.e., A. O. C. S. Official Fuller's earth and N. S. P. A. Official activated clay. He was fortunate in obtaining two gal-

TABLE III

Analysis of Two Heavily-damaged 1942-43 Crop Soy Oils and the Response of Derived Refined Oil to Various Bleaching Clays

	Oil C	Oil D
	Badly Frost-damaged Oil	Moderately Frost-damaged, then Badly Weather-damaged Oil
Crude Color, 1"	200Y 7.5R (6)	140Y 9 9R (5)
% F. F. A.	1.2	1.2
% Heat Break	0 56	0.85
Green Grade	No. 2 6	No. 1 (by wide margin)
Refining Loss (lye)	5.5% (Max.) 6 2% (⅔ Max.)	7.9 (Max.) 7.3 (⅔ Max.)
6% A. O. C. S. Bleach	280Y 7.5R (14)*	245 11.0 (9)
4% N. S. P. A. Bleach	35 3.8 (1)	40 6.5 (2)
A. O. C. S. Official Earth		
6%	280 7.5 (14)	245 11.0 (9)
9%	195 6.1 (6)	185 8.0 (6)
12%	115 5.1 (4)	165 7.1 (5)
15%	80 4.4 (4)	
18%	45 3.7	90 5.1 (4)
Commercial Earth "C"		
4%	175 5 9 (5)	185 7.5
6%	80 4.5 (4)	115 5.9 (5)
8%	40 4.0 (4)	80 5.2 (3)
10%	35 3.8 (3)	55 4 5 (4)
Commercial Earth "A"		
4%	70 10.9 (2)	60 10.2 (5)
6%	35 4 9 (1)	35 8.0 (3)
9%	25 2.8 (3)	25 5.5 (3)
N. S. P. A Activated Clay		
3%	40 6 5 (4)	
4%	35 3.8 (1)	40 6.5 (2)
5%	25 2.8 (3)	35 5.1 (1)
7%		25 3.7 (3)

* Figures in parenthesis after color readings represent the (net) number of color glasses used to obtain best hue match and fairly close brightness match.

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* By the time of the Fall, 1944, A. O. C. S. meeting in Chicago aging data had been submitted on a total of 7 samples of crude oil (including the earlier ones studied), and in no case was there any serious deterioration of bleaching response. These were all expeller oils and the Committee is now studying extracted and degummed extracted oils, as well as at least one hydraulic crude.

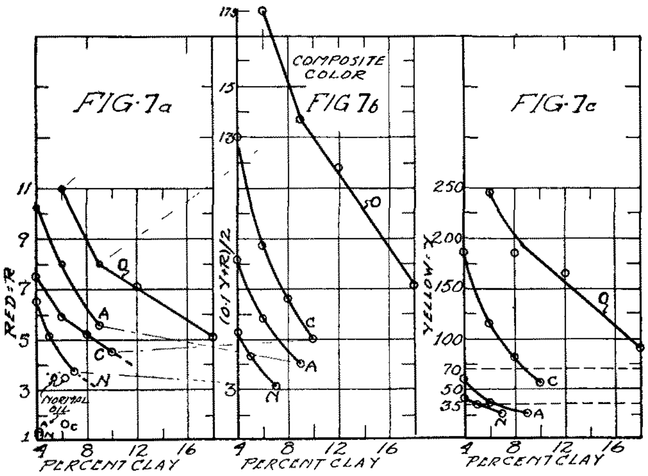

FIG. 7. Bleaching Response of Badly Frost-damaged Then Field-damaged Soybean Oil Against Four Different Clays.

Here the chlorophyll had become degraded or decomposed in connection with the weather (field) damage influence, so the red color curve for the A. O. C. S. earth is not quite as flat as in the case of oil C. On the other hand, in the range studied, earth C shows up better than earth A at all points, a misleading indication of bleaching effectiveness because in Figure 7b the two clays are shown in their true relationship, since 7b also takes account of green removal. Note the comparative remoteness of the curve for the A. O. C. S. earth from the others when both color components are considered.

lons each of two different types of off-quality oil—quite enough by running bleaches at half scale to make the study of various clays, even enough to use in a limited way in the aging study. The analysis and bleaching data on these oils are given in Table III and the latter are plotted in Figures 6 and 7.

In these results we find indications of the minimum dosages of the various clays necessary to give low enough yellow readings whereby the bleach color can be read without employing more than four color glasses. There is another important reason, however, for desiring a test earth and test dosage which will give yellow readings preferably not over 70 on all oils likely to be encountered, and that is removal of the red depressing effect associated with high yellow readings due to chlorophylls which, as just pointed out, may lead to a false evaluation of some oils.

IN JUDGING from these curves what might be considered a suitable single dosage of clay to use in a standard test, one that will give readable colors on the extremes of off-color oils down to "sample grade," the writer will say that the winter-weather damaged oil represented in Figure 7 approximated the worst quality for that type he had encountered in 1943. The green oil represented in Figure 6 was probably greener than 90% of all the oils falling in the green grade classification, but some specimens falling in the other 10% were much darker still. Nevertheless, it is believed that any test which will give 105y or less on the winter weather-damaged oil represented here would also give an easily-readable color on the darkest green oils encountered last year. If we take 105 yellow (70 y plus 35 y) as being the maximum that we would accept in the category of "easily readable color," it is found that a dosage of approximately 17% of A. O. C. S. earth would be needed for the winter weather damaged oil, and 13% for the green oil. This yellow, however, would be attained by using only 6½% of earth C on the winter weather damaged oil and 5½% on the green oil. Correspondingly smaller quantities of earth A would be needed. If we take 70 yellow as the maximum desirable, then we are forced to use a dosage of around 20% A. O. C. S. earth on the worst of these oils and 9% of earth C.

TABLE IV

Sample	A				B				C				D				E			
Lab. No.	Match		A. O. C. S.		Match		A. O. C. S		Match		A. O. C. S.		Match		A. O. C. S.		Match		A. O C. S.	
	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R
1	25	4.1	70 40	3.4 3.9	25 25	3.0 2.9	30 30	3.0 2.9	20 20	2.4 2.4	25 20	2.5 2 5	85 90	5.3 4.4†	70	5 0	35	6.3	70	6.3
2	25	3.7	35	3.7	15	2.2	20	2.2	15	2.4	20	2.2	70	4.6	70	4.6	35	6.7	70	6.6
3	30 35 25	3.0 3.2 3.0	.... 30 29	.... 3.0 2.9			AFG — RTC —		20 18	2.2 2.0	21 21	2.1 2.1			RTC — AFG —		50 35 50	6.0 6.5 5 8	59 70 56	5.9 5.9 5.6
4																				
5	70	4.0	70	4.0	35	2.9	35	2.9	35	2.6	....	....	170	5.5	70	4.5	....	....	70	7.4
6	26	2.6	26	2.6					17	1.6	17	1 7	90	4.2	70	4.4	90	5.3	70	5.4
7	70	3.3	....	....					30	1.8	....	....	95	4.9	....	....	95	5.7	70	5.3
8	25	3.2	....	....					20	1.7	....	....					....	....	70	6.6
9	70	3.7	70	3.7									Match = Matched Yellow † With White Bulb (Straight Mazda)							
10	20	2.2	....	....					15	1.6	15	1 6								
11	Collaborative Check Color Readings on Refined Bleached Soy Oil Samples (1942-1943)																			

Lab. No.	F				G				H				I				J			
					6% Off. Earth				4% Sp. Filtrol				6% Off. Earth				4% Filtrol			
	Match		A. O. C. S.		Match		A. O. C. S.		Match		A. O C. S.		Match		A O C. S.		Match		A. O. C. S	
	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R	Y	R
1	90	7.5	70	7.5	150	5.5	*70	4.7	20	2.8	28	2.6	180	7.5	70	6.4*	25	5 8	70	5.7
2	70	7.2	70	7.2																
3	105 120	7.1 7.0	 70	.... 6 2*	*35	5.2	70	4.8	20 25	2.6 2.4	25	2.4	70	6.4	70	6.4	35 45	5.5 4.8	70	4.8 ....
4					170	3 9*	70	4.2*	25	2.5	25	2.5	230	6.6	70	6.7	35	5.3	70	5.1
5	....	....	70	6.9																
6	90	7.0	70	7.0			Match = Matched Yellow * Remarked "Hard to Match"													
7	110	7.9	70	7.9																
8	125	8.2	....	....	135	6.4	....	....	....	....	20	2.1	160	9.0	....	....	....	....	40	4.3
9					170	5.1	70	4.3	35	2.8	30	2.8	170	6.7	70	5.8	70	6.0	70	6.0
10																				
11					70	4.2	70	4.2	20	2.4	24	2.4	90	5.9	70	5.8	45	5.1	70	5.2

We are so accustomed to thinking in terms of a 6% test dosage (or less) that most of us probably will object to considering anything much beyond this for a standard test. But let us be realistic about this. In the first place, as the trend in soy oil trading has been so far, we are interested not in grading prime oils, but in grading off oils, from the cut-off point designated to distinguish prime and off color, right up through the entire off-color range to the sample grade cut-off. The past year's experience, as typified by the two oils being discussed, was a costly but convincing demonstration of the range of color quality our standard bleach test will have to cover. It seems to the writer that we must make up our minds to choose a dosage close to, or slightly above, the lowest percentage which gives yellow readings below the maximum which we are willing to accept, whether this is 70 or 105 or 140 yellow—and this must be determined by reference to the worst quality oils it is intended to grade, short of "sample grade."

Moreover, it is apparent from the foregoing that the test which we must use to grade all qualities of off crude oils will not always be a suitable test for routine use by refiners and processors, who for control purposes, may want to evaluate the bleaching qualities of prime oils. Whatever clay may be chosen for the test, the dosage in which it must be used will be much too strong to afford a good grading of light prime oils, and that holds whether the test be to use 4% of an activated clay, or 18% of A. O. C. S. clay. That has been shown by the way the activated clay refined bleach colors have run on most of the 1943-44 crop oils. Since our first consideration, however, is a standard test clay for commercial grading purposes, which means for grading the *off qualities in the case of crude oil*, the clay selected and the percentage designated for crude oil grading should be chosen with that only in mind.

Also it appears that the very active clay which must be used to grade the whole range of crude oils encountered will not be suitable for grading refined oils, due to the fairly rapid deterioration of bleaching response of refined oil against the more active clays. It seems to the writer therefore that the most logical solution to the problem would be to have two different bleach tests—one, the present tentative A. O. C. S. method employing 6% Official Fuller's earth, for refined oils; another, using activated clay, for crude oils. For the evidence is clear that neither test will perform the function of the other under all trading conditions.

Inter-Laboratory Color Checks

During all of the investigations discussed here, the Committeemen gave some thought to the problem of obtaining satisfactory agreement in color readings between different laboratories. This interest was enhanced by the abnormal color properties of the season's oils notably the high chlorophyll content and associated dark green color. Our A. O. C. S. method for color, if followed literally, failed utterly to afford satisfactory color readings, whereas by using sufficient yellow glasses some laboratories were able to read colors, at least to their own satisfaction, of the order of 400 yellow, 15.0 red. However, it was not on such colors as this that our concern was based, but on serious discrepancies between different laboratories on oils with readings like 70 yellow, 6.5 red, or 35y/3.5r. To get more information on this factor the writer sponsored a series of color check samples on refined bleached oil, results on which are shown in Table IV. They speak for themselves! But the A. O. C. S. Color Committee has not been idle and by the end of the crop year its chairman had appointed three subcommittees to study various aspects of the broad problem of developing a generally more versatile and satisfactory vegetable oil colorimetry.

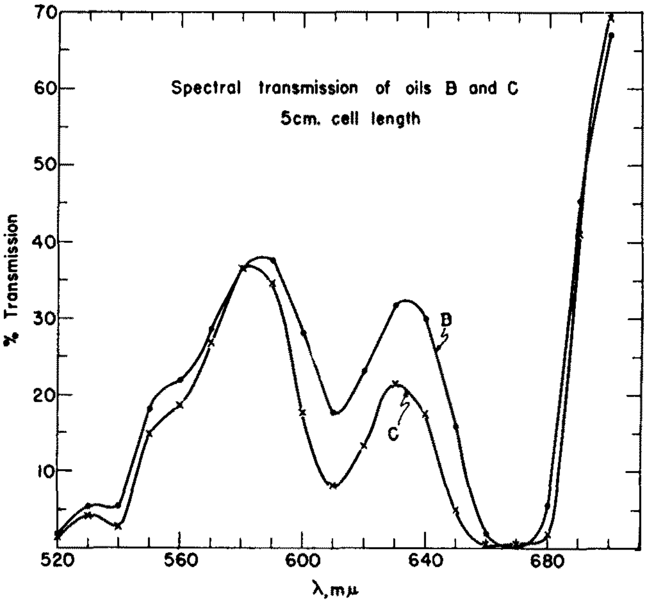

FIG. 8. Since Oils C and D (Table IV and Figures 6 and 7) were typical of two distinct types of damaged oil, and represented some of the worst encountered during the 1942-43 season, it seemed fitting to complete the description of their properties for this record by including their spectral transmission curves. Note that Oil D, the frost-damaged oil, subsequently winter-weather (field) damaged, shows a somewhat weaker absorption at 670 mμ, as well as a somewhat lower general absorption, corresponding to a degradation of its chlorophyll. These curves were obtained through the courtesy of Dr. R. T. Milner of the Northern Regional Research Laboratory.

Summary

There has been given a discussion of some important factors concerned in measuring and expressing the color of oils containing abnormal kinds and amounts of pigments. Technical problems imposed by the occurrence of a severe early frost in the Fall of 1942 are reviewed, especially as these related to the trading of soybean oil. This covers an outline of the sequence of various moves made by technical committees, with the object of adopting oil testing methods and trading rules to cover the abnormal types of soybean oil encountered during the season of 1942-43.

The inadequacy of the A. O. C. S. tentative bleach test on soybean oil to grade fairly certain abnormal types has been explained, and work leading to a new standard bleach test employing an activated clay has been reviewed. It is pointed out that the new test is to some extent limited in its applicability and cannot be considered altogether suitable for use in grading refined soybean oil; and is less desirable than the present tentative A. O. C. S. bleach test on prime and nearly prime crudes. However, it is the only kind of test available to grade damaged and off-quality crude soy oils such as prevailed in 1942-43. Mention is made of work designed to show the relation of bleach test values as obtained by the two different tests.

The question of the stability of a standard (official) bleaching clay is examined, and it is shown that activated clay and the more active natural clays are stable in activity over a period of at least a year. What had been thought at one stage of the investigation to be a loss of activity in the active clays was shown to be really a deterioration of *bleaching response* of the small lots of refined oils used in the aging studies. However, this deterioration was largely absent in the case of A. O. C. S. official earth (making it therefore the preferred earth where the grading of refined oil is concerned). Also, it is shown that soybean oil when held in the crude state does not exhibit the same degree of deterioration of the refined bleach color. There is no data available to show whether refined soybean oil held in bulk storage also exhibits a deterioration of bleaching response against highly active clays—largely because soybean oil is generally stored in the crude state.

There are presented the results of a collaborative check color reading study which show that interlaboratory checking on Lovibond colors in the case of refined bleached soybean oils is unsatisfactory in general, and this lack of good agreement in reading colors might be the cause of much annoyance in the operation of a trading rule under which refined bleach color is a factor in determining its grade.

Abstract of the Report of the Bleach Test Committee for 1943-44

THIS committee assumed a new and enhanced importance last year with the emergence of a trading rule[1] involving the refined bleached color of crude soybean oil and the designation of a standard bleach test employing activated clay. This test was devised by the Technical Committee of the National Soybean Processors' Association after some actual commercial experience had shown the inadequacy of the tentative A. O. C. S. bleach test, when the latter was used as a basis of grading crude soy oils—specifically a particular class of badly off-color oils. In the case of these oils the test indication failed to constitute a fair index to the bleaching quality. Considerable work had been done in developing the activated clay bleach test, as well as in deriving a general correlation of its indications with those of the tentative A. O. C. S. test.

Some question of the stability of the activated clay arose, and this was thoroughly discussed at a meeting of the committee in Chicago on October 6, 1943, at which a subcommittee was appointed to establish the facts concerning this question. The text of this subcommittee's report follows:

> Periodic bleach tests made in several laboratories on a more than a dozen small lots of refined soy oil comparing their responses against N. S. P. A. official clay and A. O. C. S. official earth show rather marked changes in the case of the more active clay but no significant change apparent in the case of the official A. O. C. S. earth. This indicates either that the very active clay is losing activity on aging or that changes are occurring in the oils to which the A. O. C. S. official earth is unresponsive but which inactivates the more susceptible active clay. Further work is in progress designed to show conclusively which one of these possible explanations correctly accounts for the test data given in the accompanying tables.
>
> Comparative tests also showed that no significant change occurs in the activated clay as a result of the exposure due to repeated opening of the laboratory clay container incident to normal use.
>
> The data supporting these conclusions are given in accompanying Tables Nos. 1 to 7.

A graph embodying the data from one of these tables is shown as Figure 4 in a paper by the chairman in this issue, as well as additional bleach response-time data on other bleaching clays. The change shown may be considered to be typical of that indicated by most of the data comprising the subcommittee report.

This deterioration of bleaching response between the test refined oils and the active clays (compared to the absence of such change, on most oils, in the case of A. O. C. S. official earth), which was first thought to indicate a deterioration of activity of the clay, became so pronounced and so persistent (the curves showing little tendency to level off even after many months had passed), that attention was then concentrated on attempting to establish conclusive experimental evidence that the clay was really stable in activity, rather than planning the tests to show that it may not be stable.

Thus by the time of the Society's Spring meeting in New Orleans in May, 1944, a fairly impressive amount of evidence of diverse sorts had been assembled which seemed to establish beyond doubt that the activated clay, and certain active natural clays which had been introduced into the aging studies, were indeed substantially stable in their bleaching activity, and that hence the changes indicated by the subcommittee's data were the result of changes occurring in the oils.

A meeting of the committee was held on May 11, 1944, at the New Orleans convention and so important was the material presented at that meeting in determining the interpretation of the preceding months' work that it was considered appropriate to incorporate it into a supplement report to be considered in connection with the report submitted to the Society at the New Orleans meeting.

Abstract of Interim Supplement to Bleach Test Committee Report 1943-44

THIS covers a presentation of the experimental evidence establishing the stability of the bleaching clays being studied and the significance of the subcommittee's data in light of this newer information, particularly with respect to the choice of a clay for use in a standard bleach test. The report can perhaps best be summed up by quoting its closing paragraphs:

> "In view of the findings at hand the Committee is led to the following conclusions:
>
> 1. That off-quality refined soybean oil undergoes some change on aging in containers up to one drum size,

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[1] This rule was subsequently suspended by order of the Office of Price Administration.