The Wesson Method was as modified by Dr. Mattikow, and the Chromatographic Method was carried out by the latest technique available. These results are included in Table 1. For comparison the cup losses on the oils analyzed are given. In all cases the chromatographic yields are the average of duplicate samples, and the same is true of the majority of the Wesson results.

TABLE I

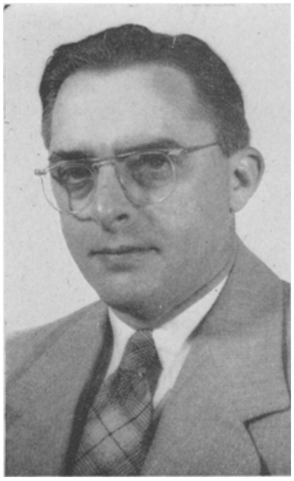
Oil	% FFA.	% Wesson	% Chromato.	% Cup.
Cotton Oil, Slow Break........	1.40	4.63	4.35	6.20
Cotton Oil, Slow Break........	1.10	2.56	2.73	5.83
Cotton Oil, Slow Break........	0.90	2.52	2.30	6.62
Cotton Oil, Slow Break........	1.20	3.45	3.61	6.76
Cotton Oil, Slow Break........	1.10	3.20	3.49	5.54
Cotton Oil, South American.	13.82	16.71	16.55	......
Cotton Oil, Expeller............	2.30	6.58	6.69	10.30
Cotton Oil, Expeller............	1.70	3.56	3.80	......
Soybean Oil, XT, Non DeG...	0.70	4.18	4.31	5.52
Soybean Oil, XT, Non DeG...	0.80	2.54	2.56	5.00
Soybean Oil, XT, Non DeG...	0.52	2.58	2.73	5.00
Soybean Oil, XT, DeG.........	0.28	0.69	0.44	1.86
Linseed Oil, Raw................	1.30	2.24	2.22	......

A careful study of the table shows that the chromatographic loss, at least in one laboratory, although usually slightly higher than the Wesson, is not so in all cases. Over-all the agreement is remarkably close. The table also illustrates the complete lack of correlation between the Wesson or Chromatographic and the cup loss.

Determinations of the percentage of neutral oil on commercial refined, washed, and dried oils have shown practically quantitative recoveries of neutral oil by both the Wesson and the Chromatographic methods. So far therefore the reason for the slightly higher chromatographic losses remains obscure. We firmly believe however that either method should prove valuable as a control for refinery operation.

Bleach and Color Methods

R. C. STILLMAN, Procter and Gamble Company, Cincinnati, Ohio



R. C. Stillman

COLOR AND BLEACH METHODS are those used to determine the amount of color in an oil, how easy it is and how much it costs to remove that color, and how much color remains in the oil after bleaching. Why do we wish to know these things? Most of the oils with which we are concerned go into edible shortenings, margarine, winter oil, etc. Consumer studies reveal that the customer likes light fat for edible purposes, and the wise producer gives the customer what she wants. Hence most oils must be bleached to a very light color for use in edible products.

In general, crude oils are sold on the basis of refining loss, refined or bleached oil colors, and flavor. The rules for trading are set up by the National Cottonseed Producers Association and the National Soybean Processors Association. These two oil trading associations accept the methods of the American Oil Chemists' Society as the basis for trading. Hence the methods of the Society must be right and must be up to date.

Most oils are yellowish-red or amber liquids. The color is due to the presence of carotenoid pigments and/or chlorophyll pigments, the latter imparting a greenish cast to the oil. The better the type of seed processed in the making of the oil, the better the color of the resultant oil. Soybeans or cottonseeds which have been left in the field after maturity or which have been heat-damaged in storage will give very dark red oils while frost damaged or immature seed will give greenish oils. The best oils are light in color, low in free fatty acid, and of excellent flavor. Such oils demand and get premium prices.

Color is hard to define and hard to measure. Few people will agree on how the color should be measured or how it should affect the price placed on a particular oil. The fact that the price of crude oils is so closely tied to its color has tended to restrict changes in the color reading methods. Hence today trading is based chiefly on Lovibond red values which, as we shall see later, are inadequate for the purpose. The Wesson method using Lovibond glasses is an abbreviated version of a method originally developed in England for measuring the color of beer. This shortened procedure has been used with questionable success for many years. It is still the official procedure of both the N.S.P.A. and N.C.P.A.

Bleaching and color reading are important laboratory methods for the control of oil processing. These laboratory methods are utilized in the trading of oils, the evaluation of bleaching earths, and the selection of earths to be used for specific purposes. The American Oil Chemists' Society has had committees working on these methods for many years. At the present time the joint effort of the Bleaching and Color Committees is aimed at an adequate solution of the color situation, which is still in an uneasy state. A whole new series of problems have arisen in the past year with the advent of color shortenings, colored synthetic granules, and other color products. These problems will open up new fields for committee study and for industrial laboratory investigations. As a direct consequence the present Color Committee is extending its work to include methods of measuring surface colors. It is with the problems of bleaching and color reading of oils only that we shall concern ourselves today.

Bleaching Methods

There are two methods of bleaching oils in general use: chemical methods and adsorption methods. Both of these methods are designed to reduce the total amount of coloring material in an oil or to remove undesirable pigments, depending upon the end-product of the process. The first method while used in the plants had no counterpart in the laboratory. In this process coloring material is removed by oxidation, which may be accomplished by air blowing, treating with an oxidizing solution, such as sodium dichromate, or by the direct addition of an organic peroxide. Since this is primarily an analytical symposium, no further time will be devoted to chemical bleaching.

Adsorption bleaching is widely used both in the plant and in the laboratory. The method involves the addition of a bleaching earth or carbon or both to the refined oil, which is then heated to approximately 115°C. and held at that temperature for about 5 min. The earth is removed by filtration. The bleaching operation is normally carried out on refined oils that have been filtered to remove refining foots which will interfere with the color removal. A.O.C.S. Methods list two tests for bleaching edible oils, one for cottonseed oil, cc 8a-52, and one for soybean oil, cc 8b-52. In the A.O.C.S. procedures A.O.C.S. natural bleaching earth is used with a 4.67% dosage for cottonseed oil and a 3.0% dosage for soybean oil. The soybean method provides for the use of 4% A.O.C.S. activated earth on green oils.

Color removal is dependent upon a number of factors including kind of bleaching material; amount of bleaching material; temperature and time, and moisture, soap, amount of coloring material, etc. In this paper only the first two factors will be considered since both bear directly upon the color measurement problems to be discussed later.

The most important bleaching material is fullers earth or clay, which is chiefly hydrated aluminum silicate. Some clays possess natural bleaching properties and are ground and used directly. Other clays are activated by treatment with acid. These clays are chiefly bentonites which have little or no bleaching power before acid treating. All of these clays, natural and activated, have their own peculiar bleaching properties, making selection of the particular earth to use of considerable importance. Cost of course plays an important role, as does the oil retention of the earth and the effect of the earth on other factors such as free fatty acid rise in the oil being bleached.

To study the efficacy of a bleaching earth some method of evaluation of the color removal is necessary. Although the problem of color measurement will be discussed in detail later in this report, we shall look at bleaching first, using spectrophotometric curves and Lovibond colors as our tools since both of these procedures are familiar to all of you. Figures 1 and 2 show the spectrophotometric curves obtained when cottonseed and soybean oils are bleached with successively increasing amounts of English earth.

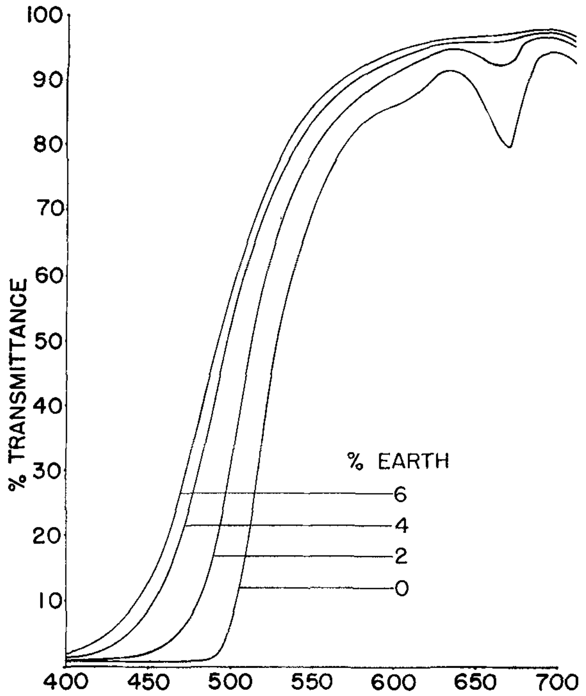


FIG. 1. Transmittance curves of cottonseed oil bleached with English earth. Measured in 50-mm. cell on Beckman B Spectrophotometer.

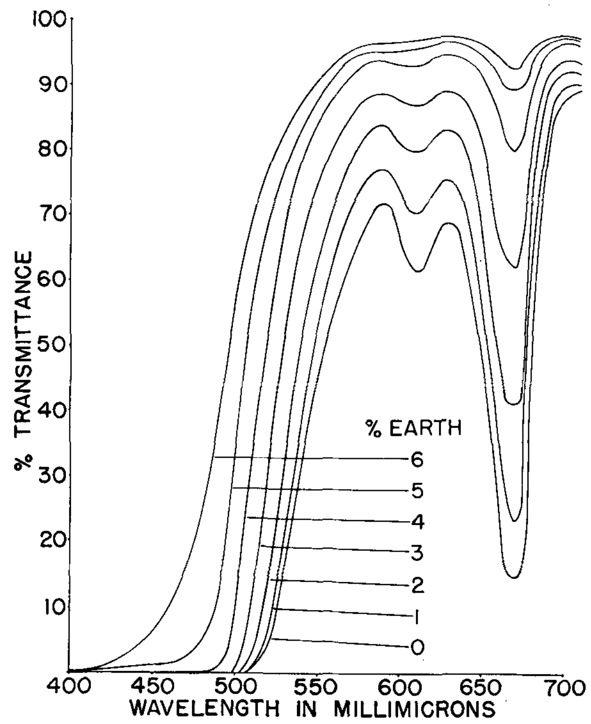


FIG. 2. Transmittance curves of soybean oil bleached with English earth. Measured in 50-mm. cell.

The absorption of light at 670 millimicrons is due to the presence of chlorophyll in the refined oils. It should be noted that, even with 6% English earth, chlorophyll is not completely removed from the soybean oil while the specific chlorophyll absorption is absent in the cottonseed oils with 4% and more earth. The chlorophyll contents of the oils have been calculated, using a procedure outlined in the October 1954 Report of the Color Committee. The procedure has since been recommended to the Uniform Methods Committee for adoption as an A.O.C.S. tentative method. The calculated chlorophyll values are as follows:

P.P.M. CHLOROPHYLL

% Earth	Cottonseed Oil	Soybean Oil
0	.131	1.54
1	.057	1.15
2	.026	.69
3	.004	.35
4	.000	.16
5	.000	.078
6		.044

It should be noted that the principal absorption of light occurs in the blue end of the spectrum. This absorption is due to the yellow-red carotenoid pigments. Reduction in the pigments due to bleaching is indicated by the shifting of the vertical transmittance lines toward the lower wavelengths. If however the transmittance curves are determined, using a 10-mm. cell, the bleaching effects become more pronounced. The curves are shown in Figure 3. The irregularities in the curves indicate the presence of more than one yellow-red pigment. In the oil bleached with 4% earth may be noted the suggestion of specific absorptions at approximately 420, 450, and 480 millimicrons. With procedures similar to that employed for determining chlorophyll it is quite possible that the carotenoid pigments could be estimated.

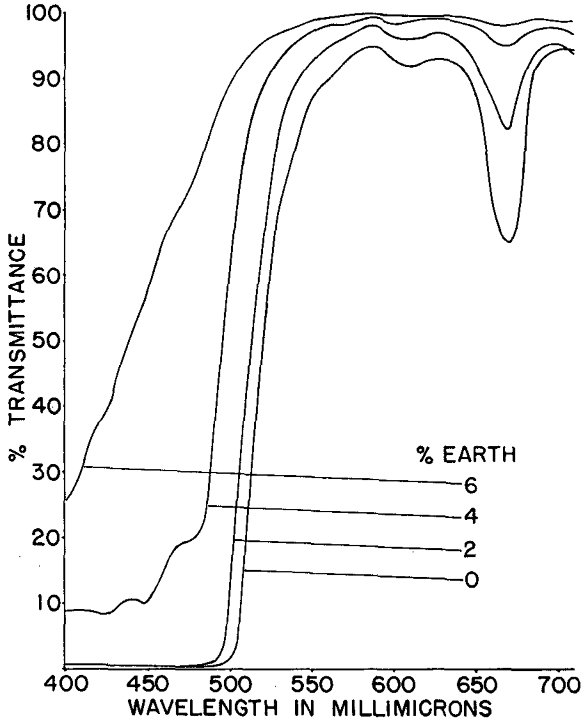


FIG. 3. Transmittance curves of soybean oil bleached with English earth. Measured in 10-mm. cell.

In Figure 4, % earth is plotted against the Lovibond colors of the bleached oils. It should be noted that while the unbleached soybean oil is darker than the unbleached cottonseed oil, soybean oil bleached with 6% earth is lighter than the cottonseed oil bleached with the same amount of earth. In simple terms the soybean oil is more easily bleached and with English earth at least will bleach to a lighter color. The apparent rise in the color of the soybean oil bleached with 1% earth is due to the chlorophyll interference with the method of color reading and will be discussed in more detail later.

The same refined soybean oil was bleached with 3% of A.O.C.S. activated earth, 3% A.O.C.S. natural bleaching earth, and 3% of a mixture of earth containing 1 part A.O.C.S. active and 2 parts English. The resultant Lovibond colors were:

Oil	Lovibond Red	Drop
Original Oil	8.1	....
3% A.O.C.S. Activated..	1.3	6.8
3% A.O.C.S. Natural	2.3	5.8
3% Carlton	2.7	5.4
3% English	5.3	2.8
3% Mix 1 A.O.C.S. Active 2 English	2.6	5.5

Obviously the most color was removed by the activated earth and the least by the English earth.

It is not the purpose of this paper to discuss the relative merits of the bleaching earths listed. Let's rather point out again that various earths have different bleaching power, different costs, different oil retentions, and different properties. The laboratory is frequently faced with the problems of evaluating these earths, and it is the tools of evaluation with which we are today concerned.

Color Methods

The A.O.C.S. method book lists four general procedures for reading oil colors: the Wesson Methods using Lovibond Glass, cc 13b-45; the Photometric Method, cc 13c-50; the FAC Method, cc 13a-43; and Gardner Standards, Ka 3-47. Most of these methods are familiar to you, and their precise procedure can be easily looked up in the methods book so only a brief description will be given here.

The Wesson method employs Lovibond glasses, and the color of an oil is compared usually in a 5¼ in. column with Lovibond color glasses, using specified yellow-red ratios. The viewing conditions are described. The method has been used for many years primarily because of its simplicity. It is still the principal method in use in the oil industry.

The photometric method was developed by the Oil Color Committee of the American Oil Chemists' Society. The method is specified for measuring the color

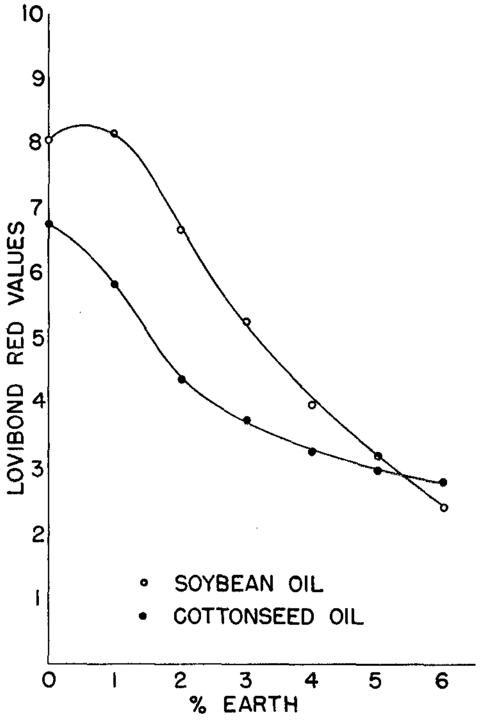


FIG. 4. Reduction of Lovibond red values with earth usage.

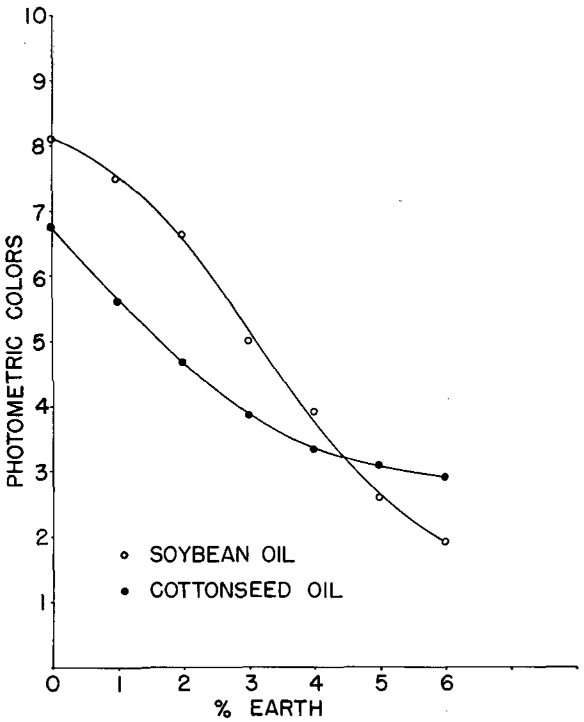


FIG. 5. Reduction of photometric colors with earth usage.

of cottonseed, soybean, and peanut oils. The instrument used is a wide band spectrophotometer. The absorbance of the oil in a 25-mm. cuvette is measured at 460, 550, 620, and 670 millimicrons.

$$\text{Photometric Color} = 1.29A_{460} + 69.7A_{550} + 41.2A_{620} - 56.4A_{670}$$

The photometric color calculation was designed to give values identical with Lovibond color values obtained, using the Wesson method. In general, the method does exactly that, but on individual oils wide discrepancies can and do occur. Such discrepancies are inevitable and have led to much unwarranted criticism of the photometric method.

The FAC method employs standard color solutions in 10-mm. tubes, against which oils in a similar tube are compared and to which numbers, equivalent to the matching standard, are assigned. The standards consist of 26 tubes in an odd numbered series, with three overlapping series, one normal, one green, and one red. Supplemental tubes for closer grading are available in some series. The spacing of the tubes is not uniform, nor was it intended that they should be. This method, which is far from precise, is used mainly for color grading of inedible oils. The method has been widely used because of its ease of application. It too has been roundly criticized, but it still remains in daily use despite concerted efforts to bring about its modernization.

The Gardner standards are used mainly in the drying oil field. These standards are patterned along the same lines as the FAC standards, but the spacings and the numbers bear no direct relationship to the FAC tubes. In the past two years some revision in these standards has been made on the recommendation of the Committee on Problem 14 of the Inter-Society Color Council. These standards are widely used and acceptably satisfactory.

So much for the methods themselves. The writer now proposes to discuss some of the broader aspects of color measurement. Some reference will be made to existing methods, their comparisons, their shortcomings, etc., but the main emphasis will be placed on what are the problems involved in evaluating the color of an oil and what is being done about the problem. First let me say that the A.O.C.S. Color Committee is studying not only oil colors but surface color measurements as well. The Color Committee and the Bleaching Committee are working jointly to achieve some measure of progress in the oil color field. Problem 14 of the Inter-Society Color Council is investigating actively "The Colorimetry of Transparent Materials." There is more than hope that something will be accomplished.

To continue our discussion of color methods let's look briefly at the Wesson and photometric methods for measuring oil colors. In Figure 4 we plotted Lovibond red values *vs.* % earth for various bleaches of soybean and cottonseed oils. In Figure 5 photometric colors are plotted instead of Lovibond colors. There are some discrepancies between the measurements, but, in general, the same conclusion concerning the bleachability of the oils would be drawn. In Figure 4 the two curves cross at about 5.25% earth and in Figure 5 at 4.5% earth. In Figure 6 the differences between Lovibond red values and photometric colors are shown. It is clear that, on the oil containing chlorophyll the photometric colors lie below the Lovibond red values. Some points are off the correlating line by as much as 0.75 color units.

The discrepancy between photometric colors and Lovibond red units and the absurdity of both under certain conditions are shown in Figure 7. Here a green oil, a red oil, and a mixture of the two are bleached and the oil color determined. It can clearly be seen that ridiculous values can be obtained by both methods, that wide variations are possible,

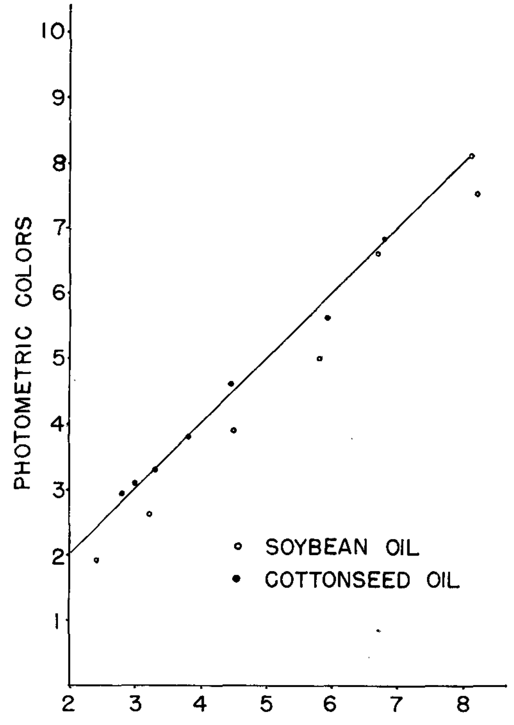


FIG. 6. Photometric colors plotted against Lovibond red values on soybean and cottonseed oil.

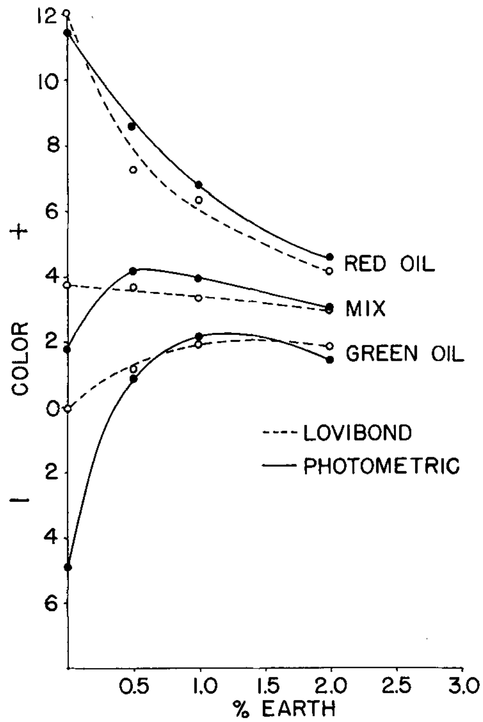


FIG. 7. Photometric colors and Lovibond red values plotted against earth usage on oils of varying greenness.

and that on green oils photometric values are below Lovibond red values and on red oils photometric values are generally higher than Lovibond values.

Let this not be interpreted as an argument in favor of one method or another. Construe it instead as an attempt to fix the facts, one of which is a just condemnation of both methods. This conclusion leaves us exactly where we were in the 1920's when the Color Committee first began its work on a spectrophotometric method for evaluating oil colors. Perhaps it is not as bad as it seems however because we know more about the measurement of color, we have better equipment available to us, and we have experienced a few hard knocks in the introduction and reception or rejection of the photometric method.

Solution of the problem is bound to be a spectrophotometric one and will probably follow one of four lines: determination of the amount and type of pigments present, or determination of the true color of the oil using the CIE system, or determination of the length of an oil column necessary to give a well defined spectrophotometric response, or some abridged spectrophotometric procedure related to the bleachability of the oil. The method for the determination of chlorophyll in oil is a definite step toward the tools necessary to solution one. Other steps in this direction will be taken even though the over-all concept may never be used.

The second concept must be investigated for a full understanding of the problem. This is the step immediately being undertaken by the joint Color and Bleaching Committee activity and by the I.S.C.C. Committee on Problem 14. The last two solutions must wait until one and two fail or indicate the desired direction to go.

Let's conclude by taking a look at what the CIE Color System can tell us. The CIE System enables us to convert a spectrophotometric curve or curves, such as were shown in Figures 1 and 2, into three values, dominant wavelength, saturation, and brilliance, the three components completely specifying any color. The details of the procedure are abundantly available in the literature, for example in Hardy's "Handbook of Colorimetry" or Judd's "Color in Business, Science, and Industry." It will suffice to indicate that a small x, y plot of the data will define hue and saturation while $\overline{Y}$ (Y bar) values will define brilliance. The system is probably familiar even though the methods of calculation may have to be studied extensively.

A plot of the x, y values of several oils studied in 1943-44 is shown in Figure 8. It should be noted that the oils follow a fairly regular pattern from the illuminant C point out nearly to the spectrum locus, where the plot breaks sharply toward the red end of the spectrum. This indicates that as the saturation of color increases, the hue shifts gradually toward the red up to about 4.0 Lovibond red where no

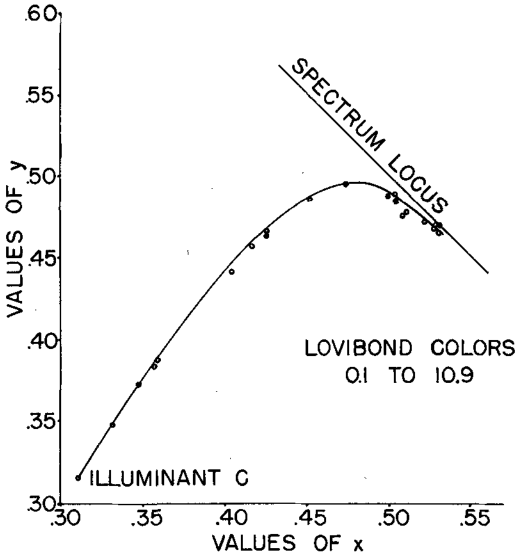


FIG. 8. Chromaticity plot of 19 oils reported in the 1943-44 Color Committee Report.

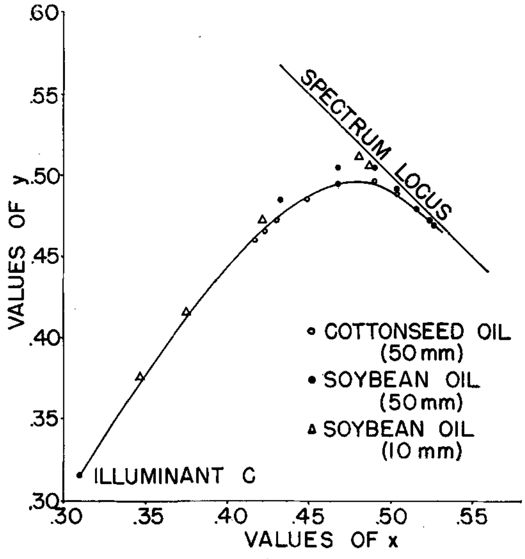


FIG. 9. Chromaticity plot of cottonseed and soybean oils bleached with English earth. Drawn curve is identical with the one in Figure 8.

further change in saturation is possible and only a change in hue can occur. From this point on the plotted line parallels the spectrum locus.

In Figure 9 the chromaticity plot of the bleached oils shown in Figures 1 and 2 is shown relative to the curve established in Figure 8. It should be noted that the bleached cottonseed oils fall nearly upon the established line but that the soybean oils lie above and to the left or green side of the plotted line. As an oil is bleached, the hue changes in the direction of lower wavelengths until a certain color is reached where litttle change in hue occurs and saturation changes rapidly.

Let's take a look at what happens to the third attribute of color when an oil is bleached. Figure 10 shows the $\overline{Y}$ values of the cottonseed and soybean oils bleached with varying amounts of English earth. The brilliance of the oils increases regularly as the color is removed, the brilliance increasing much more rapidly and to a higher value for the soybean oil.

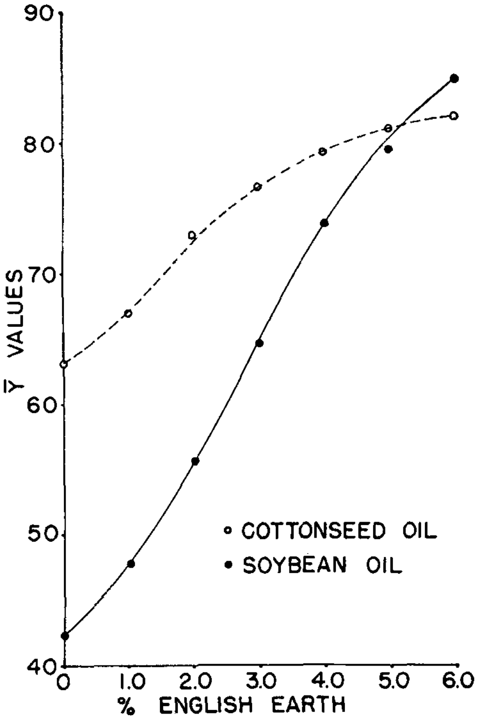


FIG. 10. $\overline{Y}$ values are plotted against % English earth.

How brilliance ($\overline{Y}$) is related to Lovibond red values is shown in Figure 11. In the figure the 19 oils shown in Figure 8 and the 14 oils from Figures 1 and 2 are plotted. It should be noted that for light oils there is a reasonably good correlation between Lovibond red values and Y values except for four unbleached soybean oils, which are quite green in hue. These four oils are as much as 4 Lovibond units below the average line.

To complete the picture, in Figure 12, the x, y values of five bleached soybean oils are shown relative to the average oil line shown in Figure 8. All of these oils are bleached with 3% of earth, but the earths are each different. The earths used are A.O.C.S. Natural, A.O.C.S. Activated, English, Carlton, and a mixture of 1 part activated with 2 parts of English. It should be noted that each of these points fall almost exactly along the same line as the oils bleached with varying amounts of English earths and shown in Figure 9.

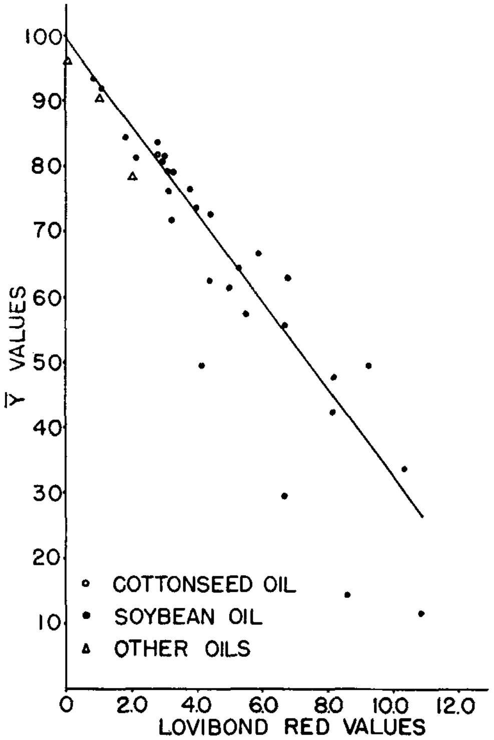


FIG. 11. Lovibond red values are plotted against $\overline{Y}$ values for a large number of oils.

What do all these figures tell us? Briefly they show us that there is a fair degree of correlation between Lovibond red values and total color as the eye sees it ($\overline{Y}$ values) except on green oils where low Lovibond values are obtained; the color of an oil follows a fairly well defined path in the chromaticity diagram regardless of whether the color is there in the original oil or whether part of the color has been removed by bleaching; there is little, if any, evidence for the selective removal of pigments by various types of bleaching earths—both the number of oils studied and number of earths are limited so

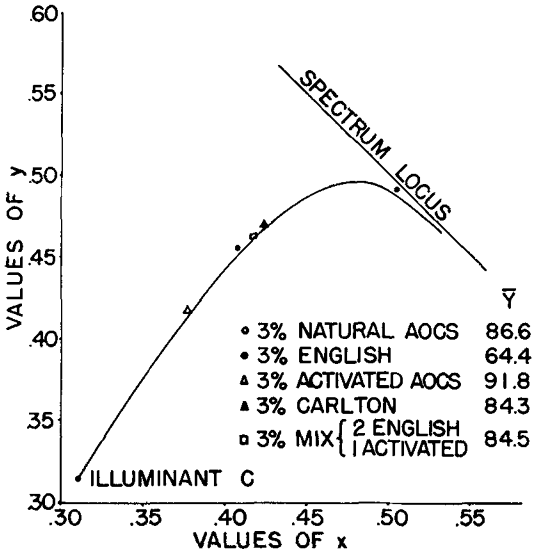


FIG. 12. Chromaticity plot of soybean oil which has been bleached with 3% of various earths. Drawn curve is identical with the one in Figure 8.

this conclusion may be erroneous; and the method has tremendous possibilities for extending our knowledge of oil colors.

We hope we have given you some insight into the Color and Bleach Method of the American Oil Chemists' Society, the merits, the shortcomings, and what still needs to be done. Perhaps the most difficult part of arriving at proper color methods is the failure of people to understand just what color is and how it should be measured. This paper may not have taught you much about color, but it will have been worthwhile if it has interested you enough to dig up the facts so you can reach your own conclusions on a scientific basis.

Melting Point, Solidification, and Consistency

HAMPTON M. SMITH, The Southern Cotton Oil Company, Chicago, Illinois

SINCE THE INTRODUCTION of the all-hydrogenated shortenings to replace the compound type, and the great increase in margarine use, methods for controlling the so-called plasticity or plastic range of the fats have been devised. The data obtained from melting points, solidification, and consistency tests are related in determining the plasticity or plastic range of the fats. Unfortunately very little published material is available however on many of these tests that are being used by the processors of fats today.

H. M. Smith

Melting Points

The melting point is the temperature at which a solid assumes the liquid condition. With pure compounds the melting point is sharp and a well defined point. Inasmuch as fats and oils are a complex mixture of compounds, they do not have definite melting points but pass through a gradual softening before becoming completely liquid; therefore the melting point must be defined by the specific conditions of the method.

The Capillary Method (1) is essentially the method used by the organic chemist for determining the melting points of the pure organic compounds. In this method capillary tubes, 1 mm. inside diameter, are filled to a height of 10 mm. with the melted fat, the end is sealed, and the fat is allowed to stand at 40° to 50°F. for 16 hrs. They are then attached to the thermometer and placed in a bath which has been adjusted to 8° to 10°C. below the melting point. The bath is heated at the rate of 0.5°C. per minute. The melting point is taken as the temperature at which the fat becomes completely clear. This method is very unreliable, and even the same operator will have trouble checking his own results.

The Wiley melting point (2) is the most widely used and gives the most useful and reproducible data of any of the methods. The determination of melts by dilatometric methods gives more accurate results, but this method is not used extensively for melting points. In the Wiley melting point a disk of the fat 3/8 in. in diameter and 1/8 in. thick is solidified and chilled in a metal form for 2 hrs. or more. The disk is then suspended in an alcohol water bath of its own density and slowly heated while being stirred with a rotating thermometer. The melting point is taken as the temperature at which the fat disk becomes completely spherical.

Most laboratories and different companies have developed their own special apparatus and operational conditions in running the Wiley melting point. Various methods of determining the end-point are in use, such as the flap-over, tapping the sphere, which if it is at the end-point, will return to its spherical shape immediately, etc. Under carefully controlled conditions an analyst should be able to check results within plus or minus 0.2°C. In order to check with other laboratories each analyst must adhere closely to the standard method.

As an example of the accuracy of the Wiley method, a series of samples were run by seven different analysts in our laboratory. Of the seven analysts only one ran Wiley melts as a routine test, and with the other six it was only an occasional operation. The results are given in Table I.

As can be seen from the above table, the average difference between duplicate samples by the same analyst is 0.2°C. The difference between the highest value and lowest value is sample number one—0.6°C., sample number two—0.6°C., and sample number three—0.4°C. While these values may not be ideal, they are within a satisfactory and useful range for control laboratory purposes.

A series of samples sent out to subcommittee members by J. P. Hughes, chairman, were run in five different laboratories. Duplicates of each sample were run by two analysts on two different days, giving a total of eight determinations from each laboratory on each sample. From the data in Mr. Hughes' report the highest and lowest values reported for sample number one are 96.8°F. and 94.3°F., sample number two—106.0°F. and 103.1°F., sample number three—125.0°F. and 118.4°F. The range of 2.5°F. and 2.9°F. on samples number one and two are within a range that would be expected. The range of 6.6°F. on sample number three is explained by the fact that it is a formulation which exhibits the phenomenon of double melting points. One laboratory obtained good checks on sample number three at around 119°F. while another laboratory got equally as good checks at around 124°F. and the other three laboratories were between these two points. The checks obtained on all samples within a laboratory were very good