Standard Potassium Dichromate

A few years ago this Committee strongly urged the U. S. Bureau of Standards to prepare and maintain a standard sample of potassium dichromate to serve as a standard for oxidimetry and iodimetry. Such a sample is now available and may be purchased from the U. S. Bureau of Standards at Washington, D. C.

Spectroscopic Methods

A subcommittee undertook to analyze a group of soap and tallow samples by the spectroscopic method of the Rubber Reserve Company. The results obtained are shown in Table 4. A committee has recently been appointed on spectroscopic methods with R. C. Stillman as chairman, and any further work of this kind will be referred to that Committee.

Tallow Refining-Bleaching Test

Work was started this year in an effort to find some better means of evaluating fats from the standpoint of color for soap production. This began with a collaborative study using a method proposed by L. B. Parsons [Oil & Soap, *20*, 256-7 (1943)]. This method is not concerned with refining loss, but only with the bleached color. The data obtained on a series of samples appear in Table 5.

These samples were bleached with an activated bleaching earth. It is evident from these data that there is no correlation between the FAC color of the original fat and the color after refining and bleaching. Further work will be done this coming year on this method.

Rewriting Methods

During the past year a subcommittee has worked extensively with the editor of the Analytical Methods in reviewing the methods of the entire section on Sampling and Analysis of Commercial Fats and Oils for the new book of methods which is in preparation.

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The Evaluation of Bleaching Earths*

The Adsorptive Capacity of Some Bleaching Earths of Various pH for Chlorophyll in Soybean Oil

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IT is generally recognized that few, if any, types of bleaching earths are equally well suited for the adequate color reduction of all kinds of oils. Nearly all bleaching-earth manufacturers produce several types of adsorbents for industry, at times recommending a particular type for a specific oil. Assuming that the bleaching-earth producers know how to prepare a type of earth which is especially suitable for a very specific group of oils, it is still almost totally unknown why an earth prepared in a specific manner is suited for one type of oil and at the same time, *ineffective* for others. It is also interesting to note that this individual suitability of bleaching earths is sometimes very selective. An earth designated by the manufacturer for one group of oils will bleach some oils of this type to a greater extent than other oils of the same type (1).

Parsons (2) suggested that the decolorization of oils by fuller's earth was due to adsorption. Subsequent work has led to the general acceptance of this point of view. Many of the earlier adsorption studies were correlated by Rogers, Grimm, and Lemmon (3) who showed that in bleaching experiments, using a number of petroleum products and several different types of adsorbents, that Freundlich's (4) equation applies accurately when the amount of color removed is used as a measure of the amount of material adsorbed.

In attempting to follow this procedure in the decolorization of vegetable oils, one is confronted with the problem of determining the true color of the unbleached and bleached oil. Obviously, the Lovibond system of color matching, as is universally used today in the vegetable oil industry, is inadequate in this respect for it is impossible to obtain a satisfactory match by a combination of red and yellow glasses for an oil, such as soybean, which contains varying amounts of red, yellow, and green pigments (5). The values of a true color must be additive in the sense that the color, C_m of a mixture of two oils having colors C_a and C_b will be given by the equation:

$$C_m = \frac{C_a V_a + C_b V_b}{100}$$

where V_a and V_b respectively are percentages (by volume) of the oils whose colors are C_a and C_b (6). Therefore, in the present work, observations have been confined to the chlorophyll band of the spectrum, whereby more accurate and comparative values could be obtained spectrophotometrically to satisfy the conditions of the above equation.

The chemical properties of bleaching clays, natural and artificially activated, as well as activated carbons, have been studied extensively by many investigators, and it has been generally concluded that in most instances the bleaching action must be determined empirically because there appeared to be no definite relationship to chemically determinable values.

Parsons (7), however, in discussing the properties of fuller's earths, pointed out that all earths which had been found valuable for bleaching showed a distinct so-called "acid reaction." If a wetted sample was touched to neutral litmus paper, the paper turned

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red. If the clay was suspended in water and phenolphthalein added, a quantity of alkali, which varied widely with different earths, could be added before the red color appeared. It was concluded that this property was no indication of true acidity as the earth contained no acid; that the same power which enabled the earth to adsorb basic colors also enabled it to adsorb true bases and to prevent their reaction becoming evident until the adsorptive power of the earth had been satisfied. Parsons further suggested that the degree of "acidity," or adsorptive power for bases in solution in water was no definite criterion of the power of the earth for adsorbing bases or colors from solutions in oil. Accordingly, the bleaching power of fuller's earth for oils was by no means proportional to the ability of the earths to remove bases in solution in water although it was noted that those earths which showed the highest adsorptive power for bases were also those which had the strongest bleaching action.

Generally, it has been an accepted fact in the industry that in order effectively to decolorize oils, such as soybean, containing relatively high concentrations of chlorophyll, the so-called "acid earths" must be used in the bleaching process. Similarly, it was recently shown (8) that better decolorization of coconut oil was obtained using low pH carbons. A similar trend was observed in the bleaching of cottonseed oil with different commercial brands of active clays.

THE present work, confined to the removal of the chlorophyll pigments in soybean oil by various bleaching earths, endeavors to study the selective adsorption capacity of various commercial earths as related to some chemically determinable factor.

Refined soybean oil, extracted type, was bleached in vacuo for 30 minutes at 110°C. under controlled conditions of pressure, and agitation, with various concentrations of commercial bleaching earths, arbitrarily selected from those being currently marketed to include both natural and chemically activated types. The bleached oil was analyzed spectrophotometrically and the Lovibond color determined on a best-match basis. From the spectrophotometric data the chlorophyll density was calculated according to Beer's Law.

Using a 6% suspension of the earth in distilled water, the total titratable hydrogen for the acid earths and hydroxyl in the case of earths of alkaline pH, was determined with standardized base and acid. The so-called "free" H and "free" OH of the earths were calculated from the original pH of the suspensions. All pH readings were determined with a Beckman pH meter fitted with a suitable extension so that all determinations could be made on the suspensions directly, without reducing their volumes. The difference between the total titratable and the "free" H or "free" OH is assumed to be adsorbed by the earth and was calculated on a mol per gram basis for convenience (9).

It must be emphasized before considering the results of this investigation that the data presented were determined on samples of the same extracted soybean oil.

TABLE 1

Decolorization of Extracted Soybean Oil, Using Various Percentages of Different Commercial Bleaching Earths

Earth	% Used	Lovibond		Chlorophyll Density
		Yellow	Red	
A	1.0	35	3.0	0.18
	1.5	35	2.1	0.090
	2.0	20	1.8	0.041
B	1.0	35	3.9	0.40
	2.0	35	2.8	0.16
	3.0	25	1.7	0.071
	4.0	20	1.6	0.037
C	2.0	35	2.3	0.53
D	2.0	35	3.9	0.75
E	1.0	70	7.2	0.58
	2.0	35	4.8	0.43
	4.0	35	2.3	0.19
	6.0	35	1.7	0.093
Original Oil		70	7.7	0.80

Table 1 shows the decolorization of this oil with various percentages of different commercial bleaching earths. It is evident that the Lovibond color on a best-match basis is not indicative of the chlorophyll concentration in the oil and cannot be used to determine the adsorptive capacity of an earth for this pigment. For example, a 4% bleach using E was equivalent to 2% of C as measured by the Lovibond system; whereas the chlorophyll density of the bleached product was 0.19 and 0.53, respectively. Thus, under these conditions, approximately 76% of the original chlorophyll concentration in the original oil was removed by E while C removed only 35%. Similarly, using 1.0% of A reduced the initial concentration of this pigment about the same magnitude as the 4% bleach of E, yet the former color was 0.7 red darker than the latter in the Lovibond scale. The data are inadequate to explain these differences, but it appears in the latter case, that while A on a weight basis was most effective in chlorophyll adsorption, the increased concentration of E removed other pigments. In the former example, the presence of chlorophyll apparently depressed the red color reading, as determined in the Lovibond system.

The removal of chlorophyll from the oil by these earths follows Freundlich's adsorption equation. This equation states that the amount of color adsorbed by a gram of earth (x color units divided by m grams) equals the product of the final concentration left in solution (C color units) raised to a certain power (n) multiplied by another constant (K). Writing this equation in logarithmic form:

$$\log \frac{x}{m} = \log K + n \log C$$

This is an equation for a straight line, where n is the slope of the line, log K is the intercept on the y axis, and K is the number of color units each gram of earth would hold if the final concentration of color in the oil was reduced to one color unit. The adsorption isotherms, developed from this equation for several of the earths investigated, are presented in Figure 1.

The chlorophyll density as calculated from the spectrophotometric data has been used as a measure of color without further conversion since it satisfies the definition of a true color, discussed previously. In applying Freundlich's equation, the amount of chlorophyll removed was used as a measure of the amount of material adsorbed by the earth. It is evident from these isotherms that each earth exhibited a different adsorptive capacity for chlorophyll, but since the isotherms are parallel this difference could be attributed to a variation in the number of active centers on the earths, i.e., the earth with the greatest capacity having the greater number of active centers

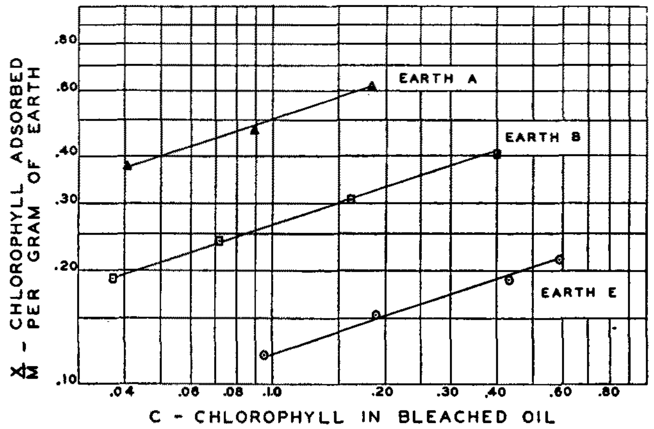

FIG. 1. Chlorophyll adsorption by different bleaching earths.

(4), and indicates that the active centers are of the same type.

Furthermore, inasmuch as the slopes of these isotherms are equal, the adsorptive capacity of these earths for chlorophyll is inversely proportional to the constant K in the equation. For example, the following equations have been derived for these earths:

$$\begin{array}{ll} \mathrm{E} & x/m = .25\,C^{1.5} \\ \mathrm{B} & x/m = .58\,C^{1.5} \\ \mathrm{A} & x/m = 1.10\,C^{1.5} \end{array}$$

showing that earth E has approximately one-fourth, and earth B one-half the bleaching capacity of earth A for chlorophyll. This has been substantiated experimentally for it required 4, 2, and 1% of these earths respectively to reduce the chlorophyll concentration of the original oil about 78%.

TABLE 2

Original pH and Calculated H or OH Adsorbed for Different Commercial Bleaching Earths

Earth	pH	Adsorbed H (Mol/Gr.)	Adsorbed OH (Mol/Gr.)
A	3.04	3.49×10^{-4}	....
B	3.10	1.86×10^{-4}	....
C	3.10	0.666×10^{-4}	....
D	7.40	....	0.049×10^{-4}
E	7.74	....	0.819×10^{-4}

TABLE 2 shows the original pH of a 6% slurry of the different bleaching earths in distilled water, and adsorbed H or OH based on the titratable ion, and the concentration of these ions as calculated from the initial pH. Comparing the chlorophyll removal efficiency of the various earths, it appears that although the trend is toward better decolorization at the lower pH values, this efficiency is not a function of pH. For example, the earths tested arranged themselves in the order of ascending pH value as A, B and C, D, E. When these same earths were used in bleaching extracted soybean oil, at 2% concentration, their apparent value as measured by chlorophyll removal is A, B, E, C, D; thus showing that pH values give no real information of the bleaching capacity of an earth for chlorophyll.

If, however, these earths are arranged in the order of magnitude of mols H or OH adsorbed, the sequence is similar to that obtained for chlorophyll removal.

Figure 2 shows in more detail this relationship between the chlorophyll and the ion adsorption. This graph was developed from the chlorophyll density as determined on the decolorized oil, and the calculated H or OH adsorbed equivalent to the concentration of the bleaching earth used. It should be emphasized before considering these data, that the values apply only to the action of bleaching earths on the chlorophyll component in soybean oil. They were not applied, for example, to the over-all decolorization of the oil.

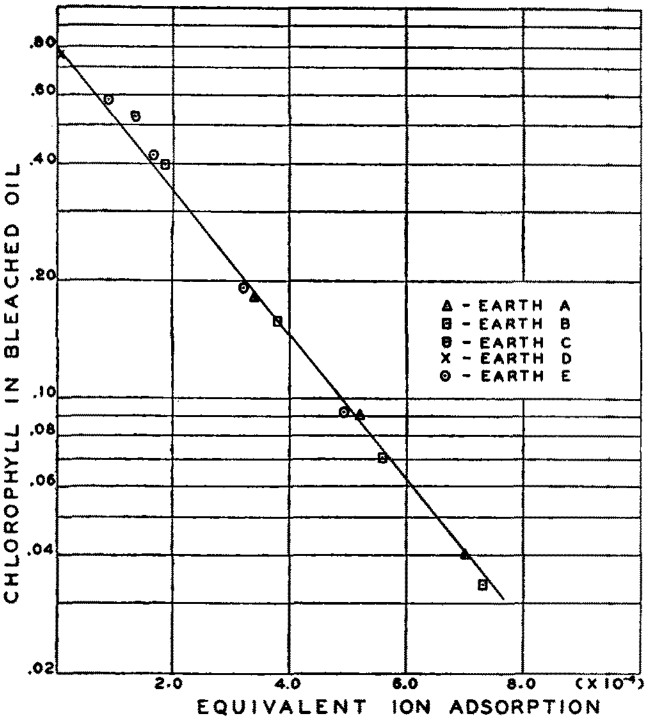

FIG. 2. The relation between the chlorophyll content of the bleached oil and the equivalent ion adsorption calculated for the concentration of earth used.

The adsorption capacity of a bleaching earth for chlorophyll in soybean oil apparently is proportional to the amount of H^+ or OH^- capable of being adsorbed by the earth, determined as the difference between the total titratable and "free" ion of a 6% slurry. For example, it has previously been shown that in order to reduce the chlorophyll concentration of the original oil approximately 78%, it was necessary to use 1, 2, and 4% of earths A, B, and E, respectively. Thus B was only 50% and E 25% as effective as A. Similarly, it was found that the ion adsorption per gram of earth was approximately of the same proportion.

From this data it has been found that the chlorophyll reduction followed the empirical equation:

$$\log C_b = \log C_o - mI$$

when C_b is the chlorophyll present in the bleached oil, C_o is the original chlorophyll content of the oil, I is the "active" acid or alkali concentration of the earth, and m is the slope of the line (Figure 2).

Previous investigations have shown that the value of n in Freundlich's equation varies widely according to the nature of the oil and the method of bleaching (10). It may also follow that these factors, together with previous processing conditions to which the oil has been subjected, will have a decided influence on the value of m in the latter equation. For example, in view of the rather low magnitudes involved, it would be interesting to consider the effect which comparatively small concentrations of soap or other alkali might have on the chlorophyll removal capacity of the bleaching earths. The data are incomplete, however, for these considerations and any discussion as to the magnitude of this effect would be speculative at this time.

It appears, nevertheless, that the bleaching power of an earth for chlorophyll can be determined chemically under certain conditions and that the "acidity" of an earth, as defined in this study, is a definite and quantitative criterion for the adsorption. That within certain limits, in this study, the removal of 95% of the original chlorophyll content — the quantity of earth required to obtain a definite degree of chlorophyll reduction can be calculated providing its ion adsorption characteristics and the bleaching capacity for chlorophyll in oil at any concentration are known. Furthermore, it is possible under these conditions to determine the quantity of any earth required to remove a definite amount of chlorophyll from this same oil, by evaluation of the ion adsorption properties.

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Correlation of Keeping Properties of Shortenings With Keeping Quality of Biscuits*

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THE possibility of the development of rancidity in biscuits and crackers is a subject which has received considerable attention over a period of many years. My contact with the industry has covered the past 26 years, and during that time there has been a never ceasing effort to improve the keeping quality of these products.

Improved methods and increased care in selecting and rendering animal fats on the part of the fat producers and new methods of measuring the keeping life of the fat itself have enabled us to have more assurance in marketing the finished products. Improved methods of producing vegetable shortenings have also been introduced by the vegetable oil refiners, and these shortenings have likewise played their part in improving the keeping quality of biscuits and crackers.

A comparison of the keeping life of one particular kind of cracker made with lards of different stability will serve to illustrate the importance of controlling the quality of the shortening to be used.

In Table 1 the first column gives the keeping life of lard as measured by the Swift Stability test. Column 2 gives the keeping life of the crackers as measured on the broken-up crackers held in closed glass bottles at 125° F. Column 1 gives the number of different runs involved in each average figure.

These crackers were made in different bakeries using lards from various suppliers.

The samples made with lards keeping from five to seven hours show inconsistencies, but the general averages, considering the large number of distinct and different samples, show a very definite improvement in the keeping life of the crackers in direct relationship to the keeping life of the lard.

In another test we held sponge crackers at the elevated temperature of 125° F. and duplicate samples were held at room temperatures. These results are given in Table II.

TABLE I

Number of Samples	Keep test of lard, active oxygen	Keep test of sponge crackers, days at 125° F.
13	1 to 3 hours	30
8	3 to 4 hours	43
10	4 to 5 hours	53
6	5 to 6 hours	40
6	6 to 7 hours	48
8	7 to 8 hours	61
11	8 and above	63

TABLE II

Sample No.	Keeping time of crackers	
	Days at 125° F.	Days at room temp.
1	45	189
2	40	160
3	35	160
4	50	140
5	30	110
6	35	148
Average	39	151

These tests were started in the fall and room temperature would average about 70° F. The results indicate that we could expect the crackers to keep about four times as long under ordinary conditions as they would at the elevated temperature. Carrying this ratio back to Table I, we would expect crackers made with a 1- to 3-hour lard to be marketable for a period of something less than four months, and when made with 7- to 8-hour lard for a period of eight months. Naturally we prefer a 7- to 8-hour lard although we do not expect the goods to stay in the stores for these excessive lengths of time.

A further extension of the keeping life may be obtained by the use of suitable antioxidants or stabilizers. As an example, some of the samples reported in Table II were accompanied by other crackers using the same lards with the addition of .15% soy lecithin. These tests are shown in Table III.

Averaging these figures, we find that the addition of the lecithin has nearly doubled the keeping life, at

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