Contact Counter Current Bleaching of Vegetable Oils

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THE Counter current principle of bleaching oils by percolation has long been used. It is our purpose to make a study of this principle in contact bleaching to determine the economy that can be effected. The presence of color can be considered as due to the attractive force that an oil has for certain color bodies, a force commonly called solution. There are many solid bodies whose surfaces have attractive forces for these same color bodies, a force commonly called adsorption. If we put an adsorbent surface, e.g., fullers earth or active carbon, in contact with an oil, we have two forces, (1) solvent power of the oil, and (2) adsorptive pull of the solid surface competing for the color bodies, and these color bodies will be distributed according to the relative strength of these two forces.

If we were to place a sample of oil in a beaker having no adsorptive power and could see the individual molecules of the color bodies (Fig. 1), they would appear in the case of a lighter colored oil as in 1A, and in the case of a darker oil as in 2A. If the beaker were made of an adsorptive material such as fullers earth or active carbon, we would get a condition such as shown in 1B and 2B. In each case, some, but not all, of the color molecules are attracted to the solid surface. It should be noted that where the concentration of color in the oil is greater as in 2B, that more color molecules are attracted to the solid surface. Thus, we arrive at an important conclusion, namely, that the amount of color that is adsorbed or removed by a solid surface is directly related to the amount of color present in the liquid.

It is apparent that if we were to empty the oil out of 1B and then place the darker oil into it we would get a condition that would approach 2B. In other words after the adsorbent has done its work on the light oil as in 1A it still has reserve power for removing some color from the darker oil.

The first step in applying this principle was to take a sample of cocoanut oil and study the amount of color removed by treatment with varying amounts of (1) standard fullers earth, and (2) active carbon.

The results are given in Table I. It should be mentioned that for simplification of our graphical and mathematical calculations, only the Lovibond Red units have been utilized.*

From Table I we can calculate the amount of color adsorbed by each unit weight of carbon corresponding to various degrees of residual color (Table II). This illustrates that the darker the color of the oil, the greater the amount of color adsorbed per unit weight of active carbon. Thus, in bleaching to 3.0 red, each unit of carbon has the power to hold 50 units of red color, but in bleaching to 0.6 red, it has the power to hold only 2.8 red color units. It is apparent that we can take the carbon after bleaching the oil to 0.6 red and it still has considerable reserve power to bleach some of the original dark oil down to 3.0 red. Simple observation of the fullers earth figures show that results are not as favorable as with activated carbon.

The object of our work then, was the utilization of this reserve adsorptive power. A flow diagram is sketched in Figure 2 which shows a two stage counter current process as conducted in the laboratory.

We have tabulated below the steps involved in such a process.

(1) The unbleached oil is treated with partially used carbon and then filtered;

(2) The press cake (spent adsorbent) is rejected and the partially bleached oil is treated with fresh carbon;

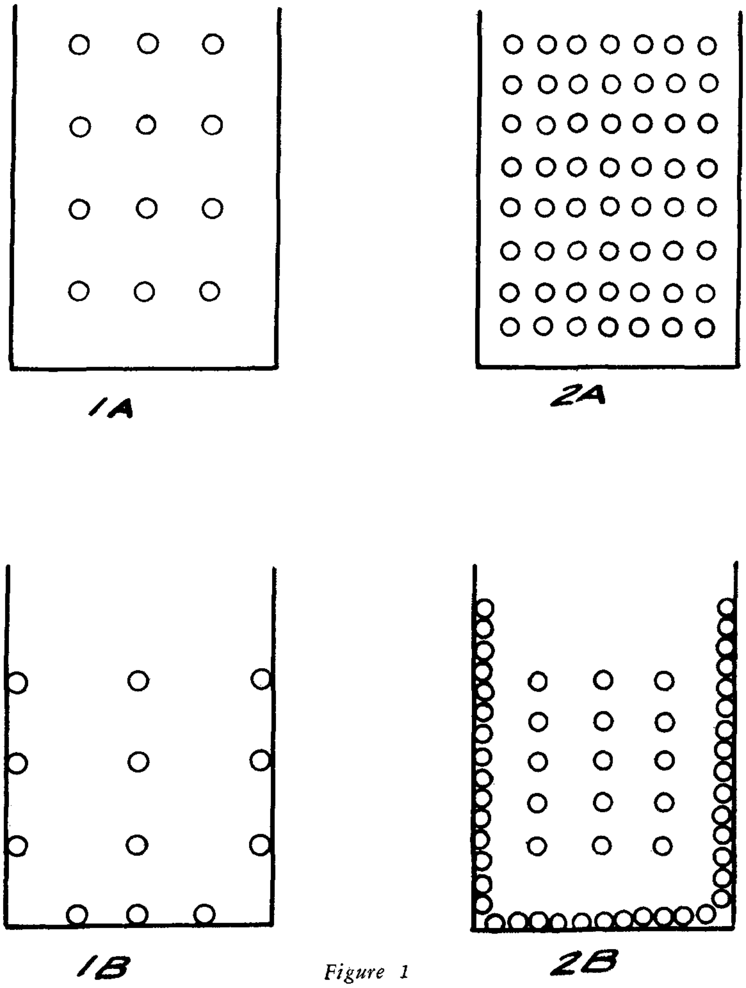

Figure 1

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* The authors appreciate that exception to this might be taken from several angles. However, this method proved itself very satisfactory in our work and introduced no appreciable error.

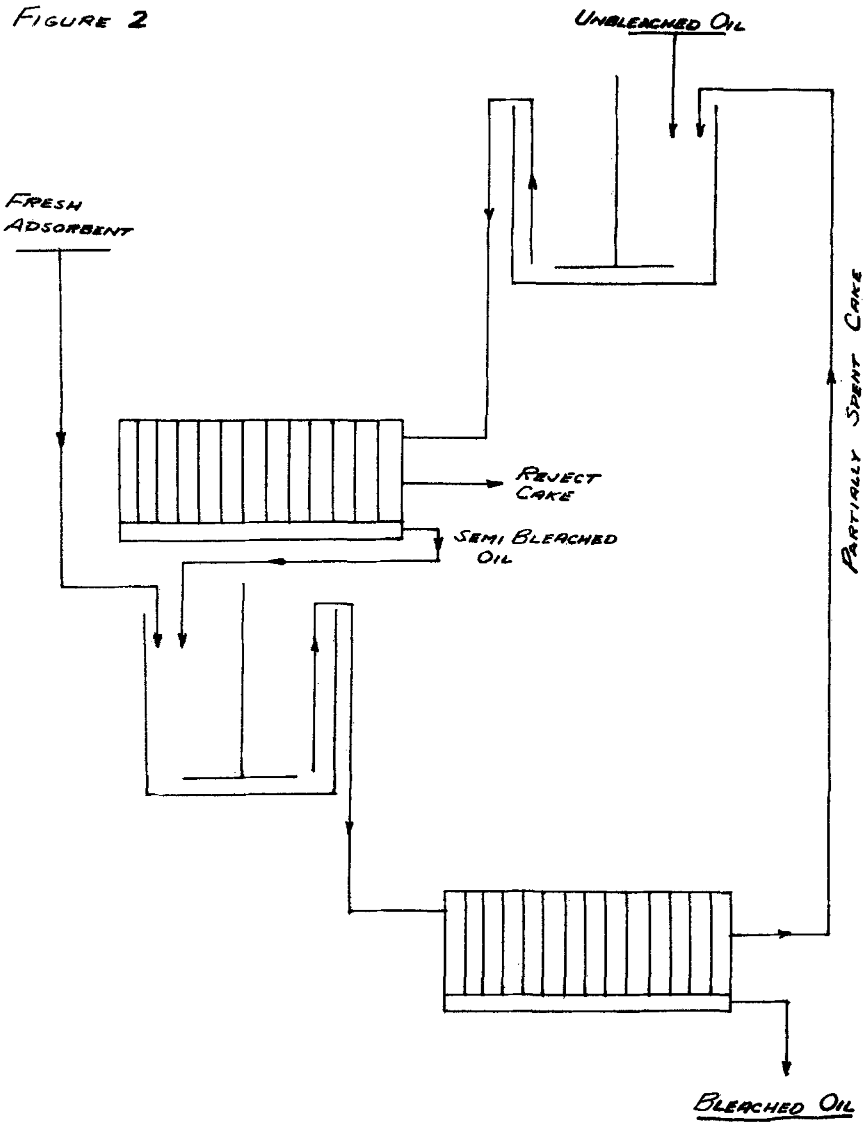
Figure 2

(3) This is then filtered giving a finished oil and the partially spent carbon;

(4) The latter supplies the adsorbent for treating a new batch of original unbleached oil. The process can be continued indefinitely.

Our interest is in finding the saving that can be accomplished by such a method over a single stage bleaching operation. It will be apparent that in order to obtain the maximum benefit, we need to select an intermediate bleached color so that the amount of new carbon required to bleach from the semi stage to the final stage, will furnish semi spent carbon with sufficient reserve power to bleach the original oil to the semi bleached stage.

The method of selecting the proper dose will be discussed later.

Meanwhile, we will give some actual results which show that conducting a two stage operation so that the intermediate color is 2.6 red (final color 1.7 red), that 0.15% active carbon was equivalent to the use of 0.25% in a single stage bleach, a saving of 40%.

In bleaching to 0.8 red final color, 0.5% active carbon in two stage use was equivalent to 1% in single stage, a saving of 50%. This illustrates that the percentage saving in adsorbent generally becomes greater where the desired final color is less.

The next work involved repetition of the previous work but using refined cottonseed oil. Using standard fullers earth, active carbon, and also a mixture of fullers earth with carbon (1:10), the steps used for cocoanut oil were repeated (Tables III and IV).

An inspection of Table IV shows that at a residual color of 2.0 Red, each unit of the earth had adsorbed 0.8 Red color and the activated carbon, 1.0 Red color. Therefore, at this desired color, the fullers earth and the activated carbon are practically the same. However, if the oil is only partially bleached, say to a color of 4.5 Red, each unit of fullers earth had adsorbed 1.2 Red, while in the case of activated carbon, this value is 4.4 Red. From this, it can be seen that the activated carbon used for bleaching down to 2.0 Red had much greater reserve power than the fullers earth for bleaching the original oil down to an intermediate color stage. Therefore, the benefits of a counter current application would be greater in the case of activated carbon than in the case of fullers earth.

It is realized that it would be impractical to use activated carbon alone on cottonseed oil, so it is of interest to see the influence of carbon in a mixture with fullers earth (ratio 1:10). Reference to Table IV shows that

TABLE I

CRUDE COCONUT OIL
COLOR — 55 Y., 6.2 R.

	Activated Carbon		Fullers Earth	
	Color		Color	
%	Y.	R.	Y.	R.
1/16	35	3.0		
1/8	20	2.5		
1/4	20	1.7	55	5.1
1/2	10	1.2	35	4.4
1.0	8	0.9	35	3.5
2.0	6	0.6	20	2.5
6.0			10	1.2

TABLE II

Activated Carbon				Fullers Earth			
% Adsorbent	Units Color Adsorbed	Color Adsorbed Per Unit Weight Adsorbent	Residual Color	% Adsorbent	Units Color Adsorbed	Color Adsorbed Per Unit Weight Adsorbent	Residual Color
1/16	3.2	51.2	3.0	1/4	1.1	4.4	5.1
1/8	3.7	29.5	2.5	1/2	1.8	3.6	4.4
1/4	4.5	18.0	1.7	1	2.7	2.7	3.5
1/2	5.0	10.0	1.2	2	3.7	1.8	2.6
2	5.6	2.8	0.6	6	5.0	.8	1.2

at a residual color of 2.0 Red, each unit of the mixture had adsorbed 1.1 Red color. This value is approximately the same as that of activated carbon and fullers earth. However, at the partially bleached color of 4.5 (referred to above), each unit of the mixture adsorbs 1.8 Red, which, referring above, is a greater value than the corresponding for fullers earth, but considerably less than that of activated carbon. This should mean that the small addition of activated carbon in a ratio of 1:10 with the fullers earth increases the reserve adsorptive efficiency of the adsorbent.

Our laboratory work conducted in the same manner as outlined for coconut oil, bears out the above statement. The figures are given in Table V.

It should be pointed out that by this counter current treatment in addition to a saving in cost of adsorbent, there is a gain in the reduced oil retention due to the use of less adsorbent.

We will not attempt to assess the value of the application of this to plant operation, as this is something that is so greatly determined by local conditions.

A rough method for determining the minimum quantity of adsorbent desirable for a two stage counter current bleaching is as follows: First, determine the amount of adsorbent required to bleach the oil to the desired final color in a single stage operation. Then take two or three percentages of this weight, for example, 50% and 70%, and conduct a laboratory two stage bleaching operation. The percentage which comes closest to the desired final color is reasonably close to the correct percentage. If greater accuracy is desired, the results that have been obtained will indicate what further dosages are to be tried.

Mathematically, the matter can be analyzed by the use of what is known as Freundlich's equation.* This equation is best employed in a graphical form which can be readily done by plotting the "color adsorbed per unit weight of adsorbent" against the "residual color."

Thus, in Figure 3, the data from Table IV has been plotted on log-log paper and it can be seen that a straight line has been drawn through each set of points. Inspection of these curves shows that the adsorption isotherm for the activated carbon (Curve No. 2) has much greater slope than that for fullers earth (Curve No. 1). Addition of carbon in a ratio of 1:10 with the fullers earth (Curve No. 3) yields a curve of considerably increased slope over the fullers earth curve.

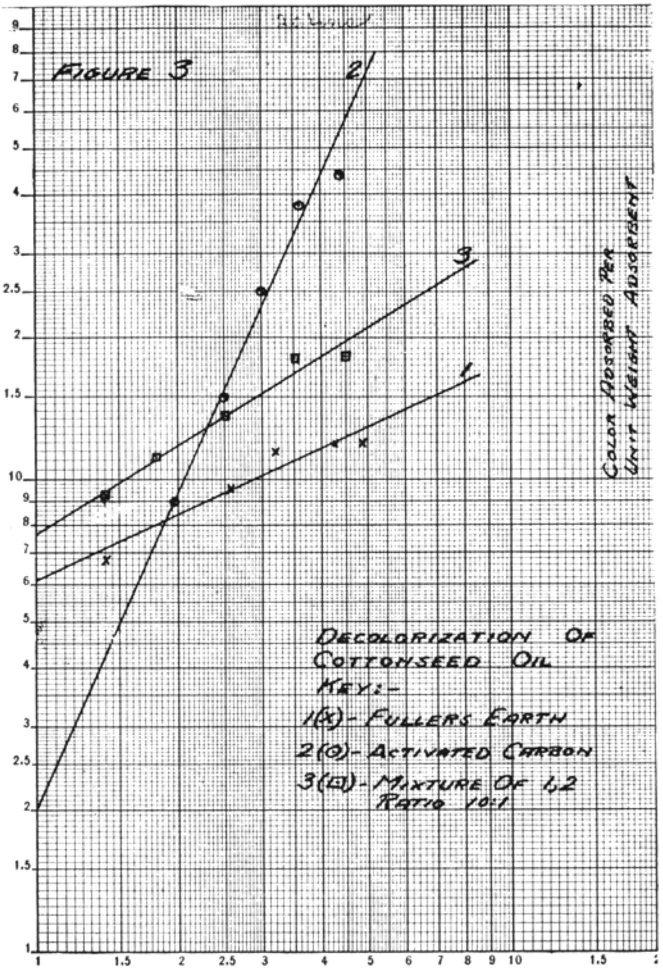

TABLE III

REFINED COTTONSEED OIL
COLOR — 25 Y., 5.5 R.

	Activated Carbon		Fullers Earth		Fullers Earth-Activated Carbon Mixture (Ratio 10:1)		
	Color		Color			Color	
%	Y.	R.	Y.	R.	%	Y.	R.
¼	35	4.4			.55	35	4.5
½	35	3.6	35	4.9	1.1	35	3.5
1	35	3.0	35	4.3	2.2	20	2.5
2	20	2.5	35	3.2	3.3	20	1.8
3			20	2.6	4.4	20	1.4
4	20	1.9					
6			20	1.4			

TABLE IV

Activated Carbon				Fullers Earth				Fullers Earth-Activated Carbon Mixture (10:1)			
% Adsorbent	Units Color Adsorbed	Color Adsorbed Per Unit Weight Adsorbent	Residual Color	% Adsorbent	Units Color Adsorbed	Color Adsorbed Per Unit Weight Adsorbent	Residual Color	% Adsorbent	Units Color Adsorbed	Color Adsorbed Per Unit Weight Adsorbent	Residual Color
.25	1.1	4.4	4.4	.50	0.6	1.2	4.9	.55	1.9	1.82	4.5
.50	1.9	3.8	3.6	1.0	1.2	1.2	4.3	1.1	2.0	1.82	3.5
1.0	2.5	2.5	3.0	2.0	2.3	1.15	3.2	2.2	3.0	1.36	2.5
2.0	3.0	1.5	2.5	3.0	2.9	.95	2.6	3.3	3.7	1.12	1.8
4.0	3.6	.9	1.9	6.0	4.1	.68	1.4	4.4	4.1	.93	1.4

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* Walker, Lewis, McAdams; Principles of Chemical Engineering, p. 645, McGraw Hill (1927).

Comparing these curves with the results shown in Table V, it is apparent that the slope of such a curve is a definite index of the benefit to be obtained in a counter current operation. That is, the steeper the slope of the curve, the greater are the benefits to be derived.

An inspection of the slope of the curve after a little practice and experience will enable one to determine the proper amount of adsorbent required for a two stage operation.

TABLE V

Adsorbent	Final Color Y.	Final Color R.	% Adsorbent Single Stage	% Adsorbent Two Stage Counter Current	% Saving In Adsorbent
Fullers Earth	20	2.7	2.8	2.0	28%
Activated Carbon	20	2.5	2.0	1.0	50%
Fullers Earth-Activated Carbon Mixture (10:1)	20	1.8	3.3	2.2	33%

How Accurate Must An Official Fat Stability Test Be?

Analysis of Three Year's Committee Studies of the Swift Fat Stability Test

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A tabulation summarizing the results of three years Committee testing of cooperative samples is discussed from the standpoint of the indicated precision, and it is shown that even with the liberal average tolerance of 17% of the value of the keeping times, the results of about one fourth of the laboratories reporting were outside of it. Throughout the series, four or about a third of the participating laboratories obtained consistently good results. These happened to be the laboratories which started using the method first. Of the others, two started getting good results after a bad first year, whereas two others failed to show agreement even after one or two year's previous experience. In the light of these apparent shortcomings of the method, it is discussed briefly from the standpoint of its suitability as an official method of the Society. This is suggested as being questionable, although the method in itself when used painstakingly and with especial regard to all necessary precautions has been shown to be inherently sound.

SIX years ago a paper (1) was read before this Society describing a method of estimating relative fat stabilities in which purified air was bubbled through the fat at an elevated temperature until the test fat became rancid to smell and had developed a peroxide number exceeding a certain threshhold value, which value depended on the type of fat being tested. The method possessed some obvious advantages over any previously known, and a committee was formed to try it on cooperative samples and determine its suitability as an official method of the Society. As the results of this investigation were not particularly good, the committee recommended further study. The next year the results were no better, but the committee recommended adoption as a tentative method and a continuation of the investigation. The Society, however, did not vote for tentative adoption, but for further work on the method. After the third year the committee again recommended its adoption as a tentative standard method, although the results were about the same as before. That year's report recapitulated the three years' work. Although any one laboratory might consistently obtain concordant results, the Uniform Methods and planning Committee disliked to recommend to the Society to adopt (even tentatively) as official, a method which had repeatedly shown certain shortcomings when the agreement between different laboratories on cooperative samples was so uncertain. Such recommendation was therefore again withheld but the committee was continued to perform further work.

Subsequent committees failed to produce any useful data and nothing further has been accomplished. After even a conscientious attempt at progress had thus died I suggested to the Uniform Methods and Planning Committee that it might reexamine its attitude on this test and determine if perhaps the interest of the Society might not best be served by having in its tentative and official methods, one, while far from ideal, is nevertheless considering many factors, still about the best that has been proposed. As a preliminary to this, I was asked to review the work of the former Stability Committees and present to the Society the situation as it now exists. I shall therefore give you an analysis that I have made of the Stability Committees' three seasons of productive work, together with their opinions and recommendations, and finally outline what appears to be a logical next step if the membership indicates that it considers an official fat stability test to be a desirable addition to its methods even if the test leaves much to be desired.

Table I reproduces the results of three years of cooperative testing, with the addition of my analysis of the indicated precision. The tolerances taken as the basis of the latter are entirely arbitrary and represent only what might be considered as reasonable on the basis of the cooperative data at hand. These tolerances were varied somewhat to fit the data on the individual samples. For example, remembering that the results are reported only to the nearest whole hour of indicated accelerated keeping time, if this time should average say 5½ hours on a certain sample (A), and if we take 15% of the average time as our reasonable allowance, we would have ±0.8 hour, or say 1 hour as the allowance. This would require that accepted values be either 5 hours or 6 hours. On the basis of the data reported,