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## Factors in the Decolorizing of Tallow. II. Oxidation

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HIS IS THE SECOND of a series of articles describing the various factors involved in the commercial decolorizing of tallow. The first of the series appeared in the September 1954 issue of the Journal (7) and described the effect of adding water with the decolorizing adsorbent. Oxidation, the factor covered in the current article, plays an important role in decolorizing tallow. Unfortunately the reactions of oxygen with the fat are complex, and the resulting effect on bleached color, keeping quality, and color stability of the fat is often confusing and unpredictable. A striking parallel on vegetable oils illustrates this. King and Wharton (6) report that in decolorizing oils there are four reactions, two working in favor of color reduction and two working against it. The two factors working in favor of it are the decolorizing action of the adsorbent and the reduction in color by oxidation of some of the color bodies, such as the carotenoid pigments. Working against it are the "setting" of other color bodies, so they cannot be removed by the adsorbent, and formation of colored compounds from colorless precursors, both as the result of oxidation.

It was the purpose of the work involved in this article to study the results of oxidation in a number of phases of tallow decolorizing and, if possible, achieve a better understanding of its basic mechanics as well as its effects. Included among the phases studied herein are storage of fat before decolorizing, amount of fat decolorized, agitation rate during decolorizing, vacuum vs. atmospheric decolorizing, and plant vs. laboratory decolorizing.

## Storage of Fat Before Decolorizing

Work published on vegetable oils indicates that the oil, particularly after neutralizing, deteriorates in decolorizing response when stored (4). To express it differently, when oil is stored, its bleached color progressively darkens; the bleach test is assumed to be carried out each time under the same conditions and with the same dosage of adsorbent.

The effect of storage upon animal fat was studied first by drying a freshly rendered lot of Fancy Tallow A, clarifying it by mixing 0.5% diatomaceous earth with 100-lb. batches at 125°F. under vacuum (7 mm.) for one hour, then filtering. A portion of the tallow was stored in a closed 5-gal. can at 120°F., and samples were withdrawn from the can at the start and after 1 and 5 days, respectively. These were decolorized with varying dosages of A.O.C.S. Official Activated Bleaching Earth (hereafter referred to as A.O.C.S. Activated Clay) to obtain complete bleached color-dosage curves.

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  - [Received November 14, 1957]
- The following modification of A.O.C.S. Official Method Cc 8c for bleaching tallows, greases, and other animal fats was used.
  - a) First 300 g. of melted tallow at 120°-130°F. are added to the refining cup specified in Method Cc 8c, followed by the adsorbent.
  - b) Employing the equipment designated in the A.O.C.S. method, the fat is agitated at  $250 \pm 10$  r.p.m. throughout the bleach.
  - c) Heat is applied, and the temperature is increased to 250°F. in 5-7 min.
  - d) Temperature is maintained at 250°F. for 15 min.
  - The fat is filtered immediately through a dry Whatman e) No. 2 filter paper, and Lovibond color is determined.

The above modified method henceforth will be referred to as the standard method. The results are given in Figure 1 and show that deterioration occurred in the decolorizing response of the fat in the five-day period of storage.

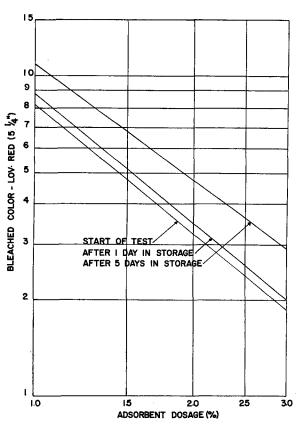


FIG. 1. Bleached color of Fancy Tallow vs. dosage of A.O.C.S. Activated Clay on unbleached fat stored at 120°F.

A second test was conducted in which 100 lb. of freshly rendered Fancy Tallow B were charged to an open steel tank equipped with steam coils, and the temperature was maintained at  $120^{\circ}-130^{\circ}$ F. by passing low-pressure steam through the coils. Samples of fat were withdrawn at the start and after 2, 3, 7, and 8 days, respectively. These were then decolorized with 2.6% A.O.C.S. Activated Clay and 5.0% of an unactivated Georgia Clay, respectively, using the standard bleaching method.

The test was repeated on the same tallow stored at  $150^{\circ}-160^{\circ}$ F. Figure 2 plots bleached color vs. time of storage at both temperatures. Progressive deterioration in decolorizing response of the tallow occurred in the case of each adsorbent at each temperature, but more deterioration occurred at  $150^{\circ}-160^{\circ}$ F. than at  $120^{\circ}-130^{\circ}$ F.

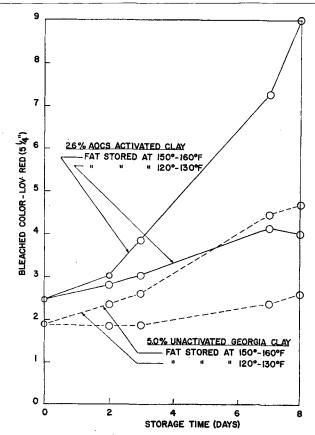


FIG. 2. Bleached color of Fancy Tallow vs. storage time of unbleached fat at different temperatures.

Analysis of the dried but unbleached tallows just prior to the tests:

	Fancy tallow A	Fancy tallow B		
Free fatty acid (% as oleic) Titer (°C.)	<b>43.0</b>	1.68 $42.9$		
Moisture (%) Color Lov. (5¼ in. col.) (Y-R)	0.20 100–19.0	$\begin{array}{c} 0.13\\ 10021.6\end{array}$		

The explanation for the effect is not certain. Freyer (4) stated that on neutralized soybean oil the effect is caused by changes in the oil during storage, also that the effect is associated with the organic peroxide content of the oil. He believed that as the peroxides build up during aging by oxidation, the decolorizing response decreases.

The writers concur that the effect is produced by oxidation and feel that, as the tallows in this work aged, one or both of the color increasing oxidative factors referred to by King and Wharton (6) prevailed over the color-decreasing oxidative factors. More specifically, either or both the setting of color and formation of colored compounds from colorless precursors by oxidation predominated over the reduction of color by oxidation. The fourth factor, or decolorizing effect of the adsorbent, is assumed to be constant.

## Amount of Fat Decolorized

The effect of the size of fat sample bleached was studied by decolorizing Fancy Tallow B with 2% A.O.C.S. Activated Clay in a series of laboratory bleaches. In each bleach test the standard method was used, but the quantity of fat decolorized was varied from 250 to 500 g.

Figure 3 shows the results, bleached color vs. size of fat sample in grams. The bleached color became progressively lower as the size of the fat sample increased, probably because of a corresponding decrease in exposure of the fat to atmospheric oxygen, thereby reducing or eliminating the color setting or color-producing factors.

## Agitation Rate During Decolorizing

A laboratory test was made in which Fancy Tallow B was decolorized by the standard method with 2% A.O.C.S. Activated Clay but the rate of agitation was varied from 100 to 300 r.p.m. in the various bleaches. This was attained by using a variable speed stirrer. The results are given in Figure 4 and show a progressive darkening of bleached color as the agitation rate increased above 150 r.p.m. Again the color increase is attributed to a greater

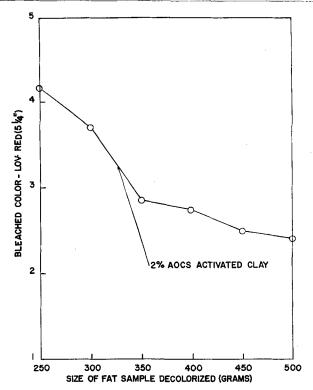


FIG. 3. Bleached color of Fancy Tallow vs. amount of fat decolorized.

TABLE I

	Plant vs. La	aboratory Decolori	zing Results					
Plant Results								
Run	1	2	3	4	5	6		
Fallow	Fancy 5 23,300 No. 1 1.50 180 120 225 230 34-6.6	Fancy 7 28.000 No. 2 0.84 105 150 225 200 33-9.3	Fancy 7 30,300 No. 1 2.00 75 105 225 230 40-4.5	Fancy 29,900 No. 1 2.00 240 80 225 225 12-1.6	Prime 11B 29,100 No. 1 1.00 90 90 220 230 35-4.1	Prime 11B 29,100 No. 2 0.50 105 135 220 200 45-5.0		
		Laboratory Results	3					
Weight of oil (g.) Adsorbent dosage (%) Contact time at max. temp. (°F.) Contact temp. (max.) (°F.) Bleached color (5 ¼ in. col.) (Y-R) Lbs. adsorbent in plant per lb. in laboratory required to reach plant color <sup>a</sup>	$300 \\ 1.50 \\ 15 \\ 235 \\ 34-7.0 \\ 0.91$	$\begin{array}{r} 300\\ 0.84\\ 30\\ 200\\ 33-10.5\\ 0.84\end{array}$	$     \begin{array}{r}       300 \\       2.00 \\       15 \\       230 \\       45-6.1 \\       0.85     \end{array} $	$\begin{array}{r} 300\\ 2.00\\ 15\\ 225\\ \cdot 15-1.9\\ 0.93\end{array}$	$ \begin{array}{r} 300\\ 1.00\\ 15\\ 230\\ 40-5.6\\ 0.67 \end{array} $	$ \begin{array}{r} 300\\ 0.50\\ 15\\ 200\\ 40-5.6\\ 0.88 \end{array} $		

degree of exposure to oxidation at the higher speed

## Vacuum vs. Atmospheric Decolorizing

Unbleached Choice Tallow, which had been stored four months, was decolorized with different dosages of a commercial activated and natural adsorbent both of Texas origin, respectively, employing the atmospheric standard method except that a temperature of 220°F. was used instead of 250°F. Portions of the same fat then were decolorized under vacuum by the method employed by King and Wharton (6) except that decolorizing was carried out at 220°F. for 15 min. Thus decolorizing temperature and time were the same in both the atmospheric and vacuum tests. Vacuum applied was approximately 1 mm. of Hg. The same procedure was duplicated on a darker fat, an undecolorized Prime Tallow, using the same adsorbents. Analysis of the tallows before decolorizing were as follows:

	Choice tallow	Prime tallow		
Free fatty acid Moisture		3.90% 0.47%		
Color Lov. (5¼ in. col.)	••• = / •	165 Y–9.9 R		

Bleached colors vs. adsorbent dosage is presented in Figure 5. It will be noted that there was little or no difference in the color of the bleached Choice Tallow whether atmospheric or vacuum decolorizing was used. On the other hand, the atmospheric procedure on the darker Prime Tallow gave consistently lighter colors than did the vacuum method. These data are the reverse of those reported by King and Wharton (6), wherein vacuum decolorizing gave lower colors throughout.

A possible explanation of the writers' findings is that, in the atmospheric decolorizing of the Choice Tallow, the color-increasing and color-decreasing oxidative factors, previously referred to, either balanced out or are all zero in value so that the decolorizing results with one dosage of an adsorbent were the same regardless of whether the procedure was carried out in the atmosphere or under vacuum. On the other hand, when the Prime Tallow was decolorized in the atmosphere, the effect of reduction of color by oxidation (e.g., fading out of yellow-red carotenoid pigments from a colored to a colorless state) predominated over the stabilization of color or formation of new colored compounds from colorless precursors, both also by oxidation. Hence, when decolorizing was carried out under vacuum, in which none of the oxidative factors exerts appreciable influence, the resulting color was darker. It follows that, in considering the relative effectiveness of decolorizing of tallow by vacuum or in the air, the nature and condition of the fat are factors.

## Plant vs. Laboratory Decolorizing

Six plant bleaches were conducted in a commercial animal fat refinery under atmospheric batch conditions. Laboratory open-cup bleaches were made on samples of the same six lots of tallow just before bleaching in the plant, thereby providing a comparison between the plant and laboratory bleached colors. In the plant the liquid tallow was pumped from storage tanks into a 35,000-lb. capacity, open bleach-tank equipped with a 62 r.p.m. mechanical agitator having four paddles on the shaft and closed steam coils. Steam was applied to the coils, the tem-

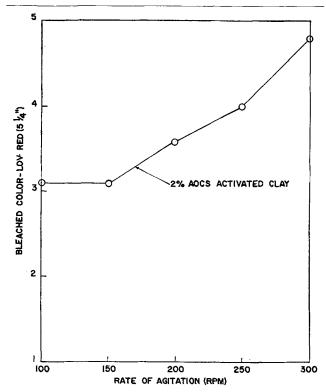
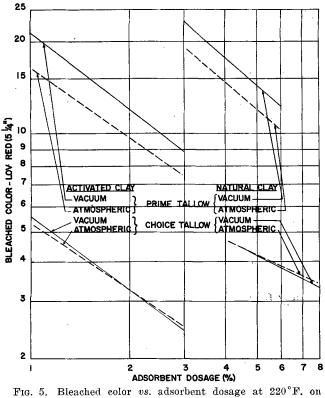


FIG. 4. Bleached color of Fancy Tallow vs. rate of agitation.

of agitation.



Choice and Prime Tallow-vacuum vs. atmospheric bleaching.

perature of the tallow was raised to approximately 220°F., and agitation and recirculation were also applied. When the tallow was dry, the adsorbent was added and bleaching was continued until the desired color was obtained on a sample of fat filtered from the fat adsorbent slurry in the laboratory. Following this, the fat adsorbent slurry was pumped through a plate and frame filter press in the plant, recirculated back to the bleach tank for several minutes to attain clarity of filtrate, and finally pumped to finished storage. The finished bleached color reported was that of the well mixed fat in the storage tank. In the laboratory tests the same adsorbent and adsorbent dosage were used as in the plant, and the decolorizing temperature approximated that employed in the plant. Other than this, conditions were those of the standard laboratory method.

Comparative bleached colors with operating condi-

# Report of the Examination Board—1957-58

URING the year ended May 31, 1958, among their various members, 41 commercial laboratories were granted Referee Certificates from the Examination Board of the American Oil Chemists Society, as follows:

- 5—Cottonseed, Oil Cake and Meal, Fatty Oils, and Tallow and Grease
- -Cottonseed, Oil Cake and Meal, and Fatty Oils 16 -
- --Cottonseed and Oil Cake and Meal
- -Oil Cake and Meal, Fatty Oils, and Tallow and 2\_ Grease
- -Oil Cake and Meal and Fatty Oils 1-
- 6-Oil Cake and Meal
- -Fatty Oils
- 1-Tallow and Grease

All laboratories certified for Oil Cake and Meal were automatically certified for Protein Concentrates.

In October, 1957, following the Cincinnati meeting, the

tions, plant vs. laboratory, are presented in Table I. It will be noted that the plant-bleached color in each of the six runs was lower than that of the laboratory. However, based upon the writers' experience, in five of the six runs, the ratio of adsorbent in the plant to that in the laboratory required to bleach to the plant color was somewhat higher than is usually obtained. No doubt this can be explained by the extended time of drying in the plant, during which the fat was exposed to atmospheric oxygen at an elevated temperature.

The poorer laboratory bleach than that of the plant probably results from the following causes: a) greater exposure of the fat to oxidation in the laboratory test, resulting from a smaller volume and more violent agitation; and b) a thinner cake thickness during laboratory filtration. The adsorptive capacity of the adsorbent is not exhausted in the bleach tank, and the filter cake imparts a substantial decolorizing effect. In the plant the filtration run starts off with no cake but may build up a cake thickness of one-half to three-quarters of an inch by the end of the operation. By contrast, the laboratory bleach has a very thin coating of adsorbent on the filter paper.

There also are factors that produce a variation in the ratio of plant to laboratory dosage to give the same bleached color. For example, plants differ from each other in operating conditions, in the size of the bleach tank, and size and type of filter press, also in bleaching equipment. Some are atmospheric batch, others are vacuum-batch, and still others are vacuum, continuous units.

### Summary

Data have been presented to illustrate the effect of oxidation in the decolorizing of tallow. In most cases the effect was detrimental to the color of the decolorized fat. However, in the case of a Prime Tallow, oxidation proved beneficial from the standpoint of obtaining a lower color.

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[Received November 13, 1957]

Examination Board completed its rules governing requirements for referee certification and revised the application blank. In addition, the Examination Board, beginning this year, will issue only one certificate per laboratory containing the names and certification of each applicant member from said laboratory.

During the year the Memphis Testing Laboratory, Memphis, Tenn., ceased operations. Referee certification of the members was withdrawn, and the cottonseed and soybean trade associations were notified.

The chairman extends his thanks to all members of the Examination Board and to R. W. Bates for their efficient cooperation.

- R. T. DOUGHTIE JR.
- E. R. HAHN
- R. R. King
- R. C. STILLMAN N. W. ZIELS, chairman