

UNITED STATES PATENT OFFICE

2,475,420

TREATMENT OF FATTY ACIDS

Alexander C. Brown and Victor J. Muckerheide,
Cincinnati, Ohio, assignors to Emery Industries,
Incorporated, Cincinnati, Ohio, a corporation
of Ohio

No Drawing. Application May 7, 1947,
Serial No. 746,624

8 Claims. (Cl. 260-419)

1

2

This invention relates to a method of producing fatty acids of improved color value, and to a method of stabilizing fatty acids against color deterioration during storage or during use.

Fatty acids are produced by hydrolyzing natural fats, that is, glyceryl esters of fatty acids, into a mixture of fatty acids and glycerine, and separating the fatty acids from the glycerine. While natural fats consist predominantly of glyceryl esters, still, natural fats also contain impurities or substances which, when exposed to heat and atmospheric conditions, become darkened in color. Also, commercial fatty acids generally are derived from the more impure, inedible oils and fats which in and of themselves are of dark color. Thus, a batch of fatty acids produced commercially by hydrolysis is usually brown in color, or darker, depending upon the quality of the feed stock put into the hydrolyzer.

In order that the color of fatty acids produced in this manner may be improved to render them acceptable for commercial usage, it has been conventional to subject the fatty acids to further treatment. One method most widely used at present to improve color has been distillation of the fatty acids under high vacuum, whereby undistillable constituents, including the dark color bodies of the fatty acids, remain in the still as a residue separate from the condensed fatty acid vapors which are now of light color. On the other hand, the crude fatty acids sometimes are bleached by addition of activated clay, carbon or bleaching earth capable of adsorbing at least some of the dark colored components, and, in some cases, both methods are utilized. For example, this latter procedure is followed in the stearic acid industry in which solid stearic acid and liquid oleic acid are obtained by separating them individually from crude fatty acids in which they are in admixture. It is desirable that stearic acid have the best possible color and a high resistance to discoloration as a large proportion of the total output finds its way into products such as cosmetic compositions and toilet preparations where appearance is of prime importance. The color of oleic acid is also important for many uses but, in general, the requirements are far less rigid than in the case with stearic acid, and oleic acid ranging in color from red to pale yellow is readily usable, whereas stearic acid must be almost water white.

The common practice in the manufacture of stearic acid is to first distill the mixed fatty acids, after which the stearic acid and oleic acid are separated either by pressing or by means of solvents. The distillation step removes a large percentage of the color, and very light colored distillates may be obtained from very dark feed stock in this manner. In fact, the initial color of the distillate is usually so light that there would

appear to be no reason to subject either of the separated products to further bleaching or distilling treatments. However, the color, though good initially, darkens during subsequent operations, or as time passes, with the result that further treatment to improve color is necessary later on, as a finishing step, if a product of best appearances is required. For this purpose, the stearic acid, which deteriorates to a lesser degree than the oleic acid, is generally bleached with an adsorbent earth or carbon, whereas the oleic acid is redistilled.

Bleaching of fatty acids is accomplished by mixing with the acid an amount of bleaching earth or carbon required to give the desired color, usually from 1 to 3% by weight, and agitating for a period of from 15 to 30 minutes at a temperature of approximately 70° C., after which the bleaching agent is removed by filtration. It is desirable that the quantity of bleaching agent be kept to a minimum, partly because of the cost of the bleaching agent itself, but primarily because of the value of the stearic acid contained in the discarded filter cake.

Although the color requirements of stearic acid are particularly important, the color of the mixed animal fatty acids, before separation thereof into solid and liquid fractions, and the color of the various vegetable fatty acids which may be employed for various purposes such as in the manufacture of soap, or as ingredients in alkyd resins, also is important in determining their ultimate usefulness and price. In many cases, the initial color of the fatty acids is of relatively less importance than their ability to retain a given color when subjected to high temperatures. Otherwise expressed, the color stability of fatty acids is of equal if not of greater importance than the actual original color.

The primary purposes of this invention have been to provide a method of producing fatty acids which are lighter in color than it has been economically possible to produce them heretofore from raw materials of equal grade, to provide a method for decolorizing fatty acids in which less bleaching agent is required to effect a given degree of color improvement, and to provide a means of increasing the color stability of fatty acids—that is, to stabilize the fatty acids against color deterioration during storage or use whether they be separated or in admixture.

This invention is based upon the determination or discovery that such results may be obtained by treating the fatty acids with adsorptive earth or carbon promptly after distillation, or at that point in the preparative cycle where the actual color value of the fatty acids is low, or at a minimum. Otherwise expressed, the invention is based upon the contemplation that freshly hydrolyzed or freshly distilled fatty acids contain

bodies or impurities of no apparent or dominant color at the time, but capable potentially of becoming discolored, and that such potential color forming bodies do in fact become discolored upon exposure of the fatty acids to heat, to atmospheric or oxidative conditions, or both. Our concept is to treat the fatty acids with decolorizing media before discoloration from such sources is developed to any substantial degree, whereby the potential source of color is removed, rather than by treating the fatty acids at some later point wherein the color deterioration has occurred and wherein the adsorptive media are expected to remove the color itself.

The precise reasons which account for the improved results cannot be stated in detail at the time; however, it is believed that freshly distilled fatty acids, although light in color, do contain substances which can produce undesirable color when exposed to heat, to atmospheric oxidation or to a combination of these factors. Such bodies, which may be termed potential color bodies, are believed to be adsorbed by the adsorptive earth or carbon and, from the results which we have had, such bodies appear to be more readily and completely adsorbed and removed than the color bodies which they produce. The term "adsorption" is intended in its usual sense in connection with this explanation, but no positive evidence is available to ascertain whether the sequestration actually is by adsorption or absorption, and it may be more proper therefore, to designate the process generally as a sorption phenomenon.

The treatment just described preferably is carried out directly or promptly after hydrolysis or distillation. For example, best results in effectiveness of the treatment are obtained when the fatty acids, immediately after distillation, are subjected to the treatment, allowing practically no time for contact thereof with air. This may be accomplished by continuously contacting and filtering the hydrolyzer output or still distillate. The degree of exposure to air and the time which may be allowed to lapse prior to the treatment with the adsorbent material, without seriously reducing the efficiency of the treatment, varies with various types of fatty acids. Thus, acids such as cotton seed or soya bean oil fatty acids, which tend to darken rapidly on exposure to air even though of light color as originally produced, are preferably treated as soon as possible, or immediately after procurement and in such manner that air contact is held at a minimum. The susceptibility of such compositions to darkening may perhaps be explained through their high content of the more highly unsaturated acids. Stearic acid may be allowed to stand in the liquid condition in contact with the air for several hours before treatment with only slight loss in the effectiveness of the treatment. Generally stated, we consider that treatment within 4 hours after completion of hydrolysis or distillation is permissible within the practice of the invention, in contrast with the 24 to 96 hours normally elapsing before decolorizing treatment in conventional practice. It is desirable also to treat the acids before the temperature has dropped below 70° C., in order to avoid reheating.

In the practice of the invention, various types of materials, commonly termed "adsorptive agents" may be employed, such as fuller's earth, activated carbon, or acid activated clay. These materials may be classified as adsorptive bleach-

ing agents, though the term "bleaching" does not properly connote the function of the agent as used in this invention since the color is not present, at least to any substantial degree, at the time the agent is added to the acid. Acid activated materials, for example, products similar to the product which is sold under the name "Filtrol," are especially effective and efficient. However, all of the materials are more effective when used according to the method of this invention than when conventional methods of decolorizing are employed. Thus, the fatty acids, when treated with earth or carbon, as indicated, rather than at some later stage in the operation when the colors have developed, become more stable against color deterioration and do not darken greatly in later stages of manufacture or in use. Also, the same amount of treating agent will yield better colors than by the process heretofore employed, or, conversely, a lesser quantity of agent, when added at the appropriate time yields an equal color value. Savings result from the use of less materials and reduced loss of fatty acids in the adsorptive earth which is discarded after treatment.

We have found the application of the method to be of particular advantage in the production of commercial stearic and oleic acids wherein mixed fatty acids derived from animal fats are normally separated by pressing or solvent separation into a solid fraction known as commercial stearic acid, and a liquid fraction known as commercial oleic acid. As previously indicated, the final color of these acids is an important factor affecting their value, the color of the stearic acid being more important than the oleic acid. In the separation of mixed fatty acids, most of the color bodies are found in the liquid acid fraction, therefore the solid acids require treatment with less earth to achieve a desired color than do the liquid acids. Hence, it is desirable to treat the solid and liquid acids individually with absorbent earth by the method described in this invention, otherwise it would be necessary to utilize a much greater quantity of absorbent earth to decolorize the mixed fatty acids to obtain stearic acid of color and color stability equivalent to that obtained by treating the stearic acid separately. Thus, a cost advantage is obtained by separating the mixed fatty acids after hydrolysis, either by pressing or solvent separation, then distilling the stearic and oleic acids separately, and promptly thereafter treating either or both distillates in the manner described. Results obtained by such procedure indicate that color forming bodies may be removed which cannot be removed in any other process of which we are aware; for example, distillation followed by decolorizing treatment as just described yields fatty acids of better color than fatty acids produced by double distillation. The significant factor, from the evidence at hand, resides in the capability of the adsorptive agent for collecting and sequestering potential color forming bodies which it could not remove after the color thereof has been developed.

In the oil, fat, and fatty acid industries colors are usually determined by the Lovibond method. By this method, the color of a column of the product being measured of either 1 inch in depth in the case of dark colors or 5¼ inches in depth in the case of light colors, is compared with the color obtained with various combinations of red and yellow standard Lovibond glasses until a match is obtained. The results are reported as

5

points of yellow and points of red Lovibond with the specified column height. For example, 20Y/5R Lovibond 5¼" column denotes that the combination of standard Lovibond glasses totaling 20 yellow and totaling 5 red provide a color match. Readings are usually reported 20/5-5¼", it being accepted practice to indicate yellow first and then red. This method is used in the following examples which illustrate our improved results.

Example I

A portion of animal fatty acids obtained by distilling animal fatty acids with steam under 35 mm. vacuum was divided into three parts. One part was treated immediately with acid activated earth; a second part was allowed to stand for 24 hours at room temperature and then treated with earth; the third portion received no treatment. The treatment in each case consisted of the use of 1% by weight of acid activated earth for ½ hour at 70° C., followed by filtration. The initial Lovibond colors were read and also the colors after heat aging for 15 hours at 100° C. The following results were obtained:

	Color Before Treatment	After Treating	After Aging
Part 1.....	15Y/3.5R	3Y/4R	15Y/2.5R
Part 2.....	15Y/3.5R	6Y/1.0R	20Y/3.2R
Part 3.....	15Y/3.5R		35Y/8.5R

These results show that treating promptly after distillation produced fatty acids having less than half the color than was obtained when the treatment was carried out after 24 hours' delay. The colors obtained after aging also show a marked improvement.

Since experience has shown that heat aging for 15 hours at 100° C. more nearly corresponds to 24 hours storage under plant conditions than does standing for 24 hours at room temperature, the fatty acids of portion 3, after 15 hours' aging, were treated with 3% of activated earth. After this treatment with 3 times the quantity of earth the color was 30Y/3.4R which is much darker than the 15Y/2.5R color obtained when the acids were treated promptly with only 1% of earth.

Example II

One sample of distilled animal fatty acids having a color of 15Y/2.6R Lovibond (5¼" column) was treated promptly with 3% of fuller's earth and a second sample was treated promptly with 1% of "Filtrol." A third sample received no treatment. The samples were aged as described in Example 1. Results were obtained as follows:

	Distilled Color	Treated Color	Color After Aging
Sample 1.....	15/2.6	12/2.0	30/4.5
Sample 2.....	15/2.6	13/1.0	30/4.5
Sample 3.....	15/2.6	13/1.0	40/12

These results show that both ordinary and acid activated earths are effective, but that the latter is much more effective.

Example III

Distilled cottonseed fatty acids having a color of 20Y/3.5R (1" column) which aged to a color of 60Y/12R (1"), were treated promptly with 1% of acid activated earth and yielded acids having a color of 7Y/1.1R which only darkened on aging

6

to 20Y/3.1R showing the effectiveness of the process on fatty acids of vegetable origin.

Example IV

The distilled animal fatty acids employed in Example 2 were treated promptly and after standing 5 hours with 1% of activated carbon. Color readings were taken after treatment and after aging. The following results were obtained:

	Distilled Color	After Treatment	After Aging
No Treatment.....	15Y/2.6R		40Y/12R
1% carbon promptly.....	15Y/2.6R	15Y/2.2R	40/5.0R
1% carbon after 5 hrs.....	15Y/2.6R	34Y/4.2R	50Y/9.0R

These results show that although carbon is not as an effective treating agent as activated earth, the improvement obtained in color stability is readily apparent.

Example V.—Soya bean oil fatty acids

Extracted soya bean oil was hydrolyzed to fatty acids by heating under pressure in a stainless steel autoclave to 250° C. with an amount of water equal to the weight of the oil. After 145 minutes' heating, the water was removed and an equal amount of fresh water added and the heating continued for an additional 30 minutes. First the water and then the fatty acids were withdrawn from the autoclave. One portion was treated immediately with 2% of acid activated earth, care being taken to avoid air contact. A second portion was held at 70° C. for 16 hours and then treated with 2% of acid activated earth. Color readings on both samples were as follows:

Treated immediately 2/6 (1")
Treated after 16 hours 12/3.4 (1")

The improvement due to the immediate treatment is readily apparent.

Example VI

Stearic and oleic acid produced by the conventional method of splitting, distilling, separating by solvents, and bleaching, were compared with respect to color and color stability with stearic and oleic acid produced by splitting, solvent separating, distilling, and then treating promptly with activated earth. The same raw materials, distilling equipment and same quantity of earth was employed. Results were as follows:

	Stearic		Oleic	
	Original Color	Aged Color	Original Color	Aged Color
Conventional method.....	2.0/3	20/2.4	20/4.5	70/43
Improved method.....	0.0/1	0.7/0.1	3/1.0	21/10.0

From inspection of these results, it is evident that the method we are proposing yields greatly improved products. Note, for example, that the color of the stearic acid produced by the improved method is better after aging than the initial color obtainable by the conventional method.

The above examples illustrate the improvement in the color and color stability of mixed fatty acids which can be achieved by our improved process.

In adapting the method to the manufacture of stearic and oleic acids involving the additional

step of separating the solid and liquid acids, we find that it is advantageous to modify the processing procedure normally used in order to take full advantage of our improved method. We have found that stearic and oleic acids of exceptionally good color and color stability can be produced if the separation step is carried out prior to distillation step. The stearic acid and oleic acid are then distilled separately and separately treated by the process of this invention. Processed in this manner, stearic acid having a color of O yellow by .4 red can be obtained, whereas conventional methods yield color of 2.5Y/5 red. An oleic acid is produced equivalent in color to double distilled oleic acid.

There are several reasons why the reversal of the normal processing steps of stearic and oleic manufacture enables us to achieve the objectives of this invention to the maximum degree. The principal reason is based upon our observations on the behavior of adsorbent agents on mixed fatty acids. We have found that there is no preferential adsorption of the potential color bodies from stearic acid as compared to oleic acid when mixtures of these acids are bleached, even though when treated separately the stearic bleaches much more readily than the oleic. As a result, when mixed fatty acids are bleached and then separated, we find that although both acids are improved in color the improvement is about equal, whereas the custom of the trade demands stearic of much lighter color than is required of the oleic. Separating of the stearic and oleic acid then distilling separately not only allows prompt bleaching, but permits of separate bleaching.

A further advantage which results from separating first, then distilling, and then treating with adsorbent agents is gained because the bleaching step then becomes the final processing step. Although prompt treatment of the distillates provides a marked improvement in stability, still with the adsorbent agents at present available, perfect results are not obtained. It is therefore desirable to avoid further treating and processing during manufacture in order that the user may derive the maximum benefit from the stabilization treatment.

Having described our invention, we claim:

1. The method of producing light-colored commercial stearic acid which comprises distilling the normally solid fatty acid fraction obtained by hydrolyzing a natural fat containing stearic acid, and removing potential color-forming bodies from such distilled fraction by treating the distillate, within about 4 hours after distillation, and before any appreciable visible color has developed therein, with an adsorbent material capable of adsorbing potential color forming bodies contained therein.

2. The method of producing light-colored commercial stearic acid which comprises distilling the normally solid fatty acid fraction of natural fats containing stearic acid, and removing potential color-forming bodies from such distilled fraction by treating the distillate, within four hours of distillation, and before any appreciable color has developed therein with an acid activated clay.

3. A method of obtaining light-colored fatty acids which comprises treating a freshly split, substantially water free, fatty acid with an adsorbent material within about 4 hours after splitting, and before any appreciable visible color has

developed in the freshly split acids to remove potential color-forming bodies therefrom.

4. A method of obtaining light-colored fatty acids which comprises treating a freshly split, substantially water free, fatty acid with an acid activated earth within about 4 hours after splitting, and before any appreciable visible color has developed in the freshly split acids to remove potential color-forming bodies therefrom.

5. In that process of deriving fatty acids from natural fats which involves the heating of the fatty acids to an elevated temperature that would normally adversely later affect the final color and color stability of such fatty acids, the improvement which comprises treating the fatty acids while they are substantially in a water free condition, with an adsorbent material within 4 hours after they have been heated to the said high temperature and before any appreciable color has been developed therein, thereby effecting the adsorption of potential color forming bodies from the fatty acids, then removing the adsorbent material and the potential color forming bodies adsorbed thereby from the fatty acids.

6. The method of manufacturing light-colored commercial stearic acid from fatty acids obtained by the hydrolysis of natural fats, said method comprising separating the solid and liquid fatty acids resulting from the hydrolysis, distilling the solid fraction, and treating the distillate within a period of approximately four hours and before any appreciable color has developed in the distillate with an adsorbent material effective to remove potential color-forming bodies therefrom before solidification of the distillate takes place.

7. The method of improving the ultimate color of commercial stearic acid obtained by the hydrolysis of natural fat, said method comprising distilling said stearic acid to eliminate non-volatile color, cooling the stearic acid to a temperature of substantially 70° C., then contacting the stearic acid with an adsorbent material within approximately 4 hours after distillation and before any appreciable visible color has developed therein, and separating the adsorbent material from the stearic acid, thereby removing with said adsorbent material the potential color-forming bodies originally present in the distilled stearic acid.

8. The method of obtaining one of the light-colored fatty acids, said method comprising pressure splitting fatty glycerides, to produce fatty acids, removing water from the split fatty acid product then treating the fatty acids so obtained with an adsorbent material within about 4 hours after splitting, before the freshly split fatty acids have fallen to a temperature substantially below 70° C. and before any appreciable visible color has developed therein.

ALEXANDER C. BROWN.
VICTOR J. MUCKERHEIDE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,608,341	Schrauth et al.	Nov. 23, 1926
2,265,020	Beach et al.	Dec. 2, 1941
2,280,842	Oliver et al.	Apr. 28, 1942
2,285,902	Christmann et al.	June 9, 1942
2,351,249	Ziegler et al.	June 13, 1944