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3,071,604

PREPARATION OF LIGHT COLORED FATTY  
ACID ESTERS

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This invention relates to a method of improving the color of esters. More specifically, this invention relates to improving the color of esters obtained from the esterification of saturated and unsaturated fatty acids with monohydric and polyhydric alcohols.

When fatty acid esters are produced, especially those produced from un-refined saturated and unsaturated fatty acids, the final ester products are often dark or discolored. What actually is responsible for the discoloration is still not too settled. There are many theories as to why color is formed in fatty acid esters, and attempts have made to determine the nature of the color. One theory advanced is that color is probably due to different color forming bodies which are usually small amounts of oxidized material derived from unsaturated bodies dissolved in the fatty acid material. These color forming bodies are often insufficiently removed from the fatty acid starting material even though the fatty acid material may have been treated for color removal.

Another theory advanced as to why color exists in fatty acid esters is that there are latent color bodies present in the fatty acids used to prepare the esters. Even though the fatty acids may have been treated to remove color, these latent color bodies which are initially colorless, will, on exposure to air and light or other atmospheric influences, markedly discolor the fatty acid material. On the other hand, there may be initially both color and latent color bodies present so that color is present even though it is not very visible in the starting material; the color being developed or increased as the latent color bodies undergo changes. Still another theory is that since color develops even though the fatty acids used have been treated to remove color, the color is due to some unknown reaction mechanism of the esterification. Therefore, what actually is responsible for the color in fatty acid esterification products is still not too settled and the fact remains that the unwanted color does develop in the final ester product notwithstanding how or why the color develops.

The problem of eliminating the color of ester material is a long standing problem in the art as indicated above. Conventional treatments, e.g., bleaching, etc., which are often employed for the removal of color brings about some improvement. However, quite often in the case of bleaching, the bleached ester often reverts to the original discoloration. Hence, in the prior art, it was necessary to treat the ester material after it was prepared, with different bleaching material, or by various purification methods. One such purification treatment is that of distillation. However, the distillation treatment is not always effective and further refining treatments may be required. These treatments are usually employed either before or after the distillation treatment in order to remove the color as completely as possible. Another treatment is by the neutralizing and precipitating action of caustic soda solution or other alkali solutions. Generally speaking, all these treatments remove the coloring material to a degree but not completely and furthermore they are costly and timely.

As indicated above, attempts have also been made to purify the starting material used in fatty acid esterifications. U.S. Patent No. 2,876,174, J. M. Preston, March 3, 1959, discloses distilling fatty acids with hypophosphorus

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acid or the alkali salt of hypophosphorus acid. The fatty acids are thus bleached and the unwanted color is apparently removed. However, when the thus treated fatty acids are used in an esterification reaction, a color nevertheless develops in the resulting ester. Therefore, as indicated above, the procedures presently employed to rid an ester of its color have not proven to be very successful; and since one of the uses of the esters is as a textile lubricant as for example, coning oils which are applied on synthetic knitting yarns, the color problem is one to be avoided. Therefore, it will be appreciated that the color and color stability of products which use these esters are of prime importance, and accordingly esters having the best color and color stability will be at a premium.

It is therefore an object of this invention to improve and stabilize the color of fatty acid esters.

It is also an object of this invention to inhibit color formation in esters obtained by the esterification of alcohols with fatty acids.

Other objects of this invention will be obvious, and will in part appear hereafter.

We have found that in the direct esterification of saturated and unsaturated fatty acids with alcohols using an acid esterification catalyst, when a small amount of hypophosphorus acid is added to the esterification system, the color of the final ester product is vastly improved as well as stabilized. We have also found that when these esters are so treated, a bleaching step or distillation step is not required to further improve the color of the resulting ester.

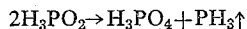
The steps involved in the practice of this invention are straightforward. A fatty acid is first dissolved in an alcohol and a small amount of catalyst, e.g., preferably an acid-containing catalyst, is added to catalyze the reaction. To this mixture is added a small amount of hypophosphorus acid. The resultant mixture is then heated for a few hours either under a vacuum or in an azeotropic system depending on the alcohol used for the esterification. Thereafter, the acid catalyst is neutralized and an ester which is substantially free of color is recovered.

The amount of hypophosphorus acid necessary for the prevention of color formation in the final ester product is usually a small amount. As illustrative of the present invention, hypophosphorus acid is added in the form of a 50 percent by weight aqueous solution of hypophosphorous acid and it is usually employed in proportions of approximately 0.05 percent to 2.00 percent based on the weight of the total reactants. Other strengths of hypophosphorus acid can also be used as for example 100% solid hypophosphorus acid. However, for convenience a 50% water solution is used. The preferred amount of hypophosphorus acid to be used is about 0.15 percent based on the weight of reactants. However, generally speaking, the amount of hypophosphorus acid to be used will depend somewhat on the amount of coloring material to be removed as well as on the conditions of operation, and may be varied with satisfactory results. Quantities less than disclosed will produce noticeable improvements in color. Thus, when hypophosphorus acid is incorporated into an esterification system, a marked improvement in the color of the esterified product occurs because the color has been inhibited and stabilized due to the reducing action of the hypophosphorus acid in the esterification reaction.

It is also to be noted that the color of a discolored ester can be removed by "bleaching" with hypophosphorus acid. This is accomplished by heating a crude fatty acid ester with hypophosphorus acid to a temperature of about 150° to 160° C., and then neutralizing with a base where-in a refined or "bleached" ester is obtained. The amount of hypophosphorus acid used is from about 0.05 percent to 2.00 percent by weight of the ester. However, the

color of the "bleached" ester is darker than the color of an ester in which hypophosphorus acid was present during its preparation.

It is believed that the hypophosphorus acid is probably decomposed to phosphoric acid and phosphine. The overall chemical reaction can be shown as follows:



Therefore, high concentrations of hypophosphorus acid should be avoided since at temperatures above 130° C., hypophosphorus acid breaks down to phosphine which is a malodorous, poisonous and a flammable gas.

The alcohols which are encompassed in the process of this invention are aliphatic alcohols such as monohydric and polyhydric alcohols having up to 20 carbon atoms in the chain. Also included are the polyoxyalkylene glycols such as polyethylene glycols and polypropylene glycols having average molecular weights of from about 100 to 2000. Other polyhydric alcohols such as glycerine, pentaerythritol and sorbitol can be used.

The fatty acids which are encompassed in the process of this invention are saturated and unsaturated mono, di and tri basic fatty acids containing from 8 to 24 carbon atoms in the chain inclusive, as for example, caprylic, capric, lauric, myristic, palmitic, oleic, ricinoleic, stearic and behenic acids, maleic and succinic and mixtures thereof including commercial mixtures thereof. We can also use dimerized acids as dilinoleic acid.

The bases which can be used in the process of this invention are organic amine bases such as triethanolamine, isopropyl amine, morpholine, etc., or inorganic bases such as alkali metal or alkaline earth hydroxides, bicarbonates and oxides as for example sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, calcium oxide, etc. These bases neutralize the acid catalyst as well as any undecomposed hypophosphorus acid and phosphoric acid that may have been formed, so that corrosion of the metal apparatus is prevented; and, also to lessen the chance of the ester being hydrolyzed by the acid catalyst which can readily take place in contact with water. The base chosen for neutralization can either form a salt with and thus precipitate the strong acid material remaining in the esterification mass and the resultant precipitated salts removed by cold filtration, as for example when inorganic bases are used, or the said acid material can be solubilized with amine bases forming amine salts which can be left in the ester without affecting the properties of the ester product and thus eliminate the need for filtration.

The acid catalysts which can be used in the process of this invention are any of the acid catalysts which are effective in esterification reactions as for example alkyl, aryl, or alkylaryl sulfonic acids which include methane sulfonic acid, benzene sulfonic acid, p-toluene sulfonic acid, dodecyl benzene sulfonic acid, etc. Inorganic acids such as sulfuric acid and phosphoric acid can also be effectively used as well as sulfonic acid-type ion-exchange resins. The amount of acid catalyst can be varied from 0.10 to 5.00 percent, based on the weight of the total reactants. The preferred amount to be used is 0.1 to 0.2 percent.

When lower chain aliphatic monohydric alcohols are used as for example butyl alcohol, amyl alcohol, octyl alcohol, etc., the esterification can be carried out in an azeotropic system at atmospheric pressure, and the unreacted alcohol and water of esterification can easily be distilled off. The alcohol that is distilled off can be recovered and re-used. When higher chain alcohols or glycols are used for the esterification, a vacuum system is required to facilitate the removal of the water of esterification by distillation; and by so removing the water of reaction or esterification, the reaction is pushed to completion.

The temperature used in the process of this invention

is from 70° to 170° C., depending on the reaction system used as disclosed above. When the reaction is carried out under reduced pressure, i.e., 4 to 60 mm./Hg, the temperature is reduced accordingly. However, the use of a vacuum system is dependent upon the volatility of the alcohol used, and as above indicated, the esterification can be either carried out under reduced pressure or atmospheric pressure. This process can be either carried out as a batch or continuous process with the proper modifications.

It must be understood that our invention is directed to the preparation of esters of improved color. The esterification reaction as well as the fatty acid esters are well known. Hence, our invention is not to be limited to any specific reactant or catalyst, but is applicable to the esterification reaction as known.

For a fuller understanding of the nature and objects of this invention, reference may be had to the following examples which are given merely for purposes of illustrations and are not to be construed in a limiting sense.

#### EXAMPLE I

282 gms. (1.0 mole) of a distilled grade of oleic acid and 400 gms. (1.0 mole) of polyethylene glycol 400 were mixed together in a suitable size flask fitted with a thermometer, stirrer and adapter for vacuum distillation. To this mixture was added 1.4 gms. (0.2 percent) based on the total weight of the reactants of para-toluene sulfonic acid monohydrate and 1.4 gms. (0.2 percent) based on the total weight of the reactants, of a 50 percent by weight hypophosphorus acid solution. The system was then brought under vacuum (30 mm./Hg), and the temperature raised to about 130°-140° C., and held there for about 2-3 hours. The water of reaction was removed by distillation from the system as it was being formed. The system was then cooled under vacuum to about 50° C. before opening to the atmosphere. The acid value of the ester was determined by titration of a sample with standard alkali to a phenolphthalein end point. If the acid value was less than 5 (indicating that 2.5 percent unreacted oleic acid remained in the system), the esterification was assumed to be complete. If the acid value was greater than 5, the amount of mineral acidity should be determined and more catalyst added if needed and the heating resumed from another hour. When the esterification was completed, sufficient triethanolamine was added to bring the pH to about 7 (neutral), thus neutralizing and solubilizing any strong acids which remain. The color of the product, i.e., polyethylene glycol 400 monooleate was 65 (percent transmission, Lumetron Colorimeter, blue filter), or Gardner 2-3.

#### EXAMPLE II

282 gms. (1.0 mole) of a distilled grade of oleic acid and 600 gms. (1.0 mole) of polyethylene glycol 600 were mixed together in a suitable flask fitted with a thermometer, stirrer and adapter for vacuum distillation. To this mixture was added 1.8 gms. (0.2 percent based on the weight of the reactants) of p-toluene sulfonic acid monohydrate, and 1.8 gms. (0.2 percent) of 50 percent hypophosphorus acid solution, based on the weight of the reactants. The system was then brought under vacuum (30 mm./Hg) and the temperature raised to about 130-140° C. and held there for about 2-3 hours. The water of reaction was removed from the system by distillation as it was formed. The system was then cooled to about 50° C. while under vacuum before opening to the atmosphere. The acid value was determined by titration with standard alkali to a phenolphthalein end point. If the acid values was less than 5 (2.5 percent unreacted oleic acid remaining), the esterification was assumed to be complete. If the acid value was greater than 5, the mineral acidity was determined, and additional catalyst added if needed and the

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heating resumed for another hour. When the esterification was assumed completed, sufficient concentrated aqueous ammonia was added to neutralize the catalyst and the resultant product was filtered to remove precipitated insoluble ammonium salts which were discarded. A yield of 860 gms. of polyethylene glycol 600 monooleate was recovered. The color was 75 (percent transmission, Lumetron, blue filter), or Gardner 2.

## EXAMPLE III

545 gms. (1.9 mole) of a distilled grade of oleic acid and 400 gms. (1.0 mole) of polyethylene glycol 400 were mixed together in a suitable flask fitted with a thermometer, stirrer and adapter for vacuum distillation. To this mixture was added 1.4 gms. (0.15 percent) based on the weight of the reactants of methane sulfonic acid and 1.4 gms. (0.15 percent) of a 50 percent hypophosphorus acid solution based on the weight of reactants. The system was then brought under vacuum and heated to about 130°-140° C. for about 3-4 hours. The system was then cooled to 50° C. before opening to the atmosphere. The acid value was then determined as disclosed in Example I above. If the acid value was found to be less than 10 (corresponds to 5.0 percent unreacted oleic acid), the reaction was assumed to be complete. If the acid value was greater than 10, to complete the reaction an additional heating cycle may be necessary. The resultant mixture was then neutralized to a neutral pH with isopropylamine to neutralize and solubilize the strong acids remaining in the mixture such as methane sulfonic acid, phosphoric acid, etc. A yield of about 900 gms. of substantially polyethylene glycol 400 dioleate product was obtained. The color was 63 (percent transmission, Lumetron, blue filter), or Gardner 3.

## EXAMPLE IV

92 gms. (1.0 mole) of glycerine, 106 gms. (1.0 mole) of diethylene glycol and 420 gms. (2.0 moles) of hydrogenated fatty acids derived from coconut oil were mixed together in a suitable flask fitted with a thermometer, a stirrer and a take-off for vacuum distillation. To this mixture was added 0.9 gm. (0.15 percent) of methane sulfonic acid based on the weight of the reactants and 0.9 gm. (0.15 percent based on the weight of the reactants) of 50 percent hypophosphorus acid. The system was then brought under vacuum (30 mm./Hg), and heated for a period of about 3 hours at 95°-100° C. and cooled under vacuum. The acid value was determined as indicated in Example I. If the acid value was less than 5, the reaction was assumed to be complete, if the acid value was not reached the heating cycle was repeated until the specification was met. The catalyst was neutralized with concentrated aqueous potassium hydroxide and about 570 gms. of mixed diethylene glycol-glycerine ester of hydrogenated coconut fatty acids was obtained. The color was 70 (percent transmission, Lumetron, blue filter), or Gardner 1.

## EXAMPLE V

275 gms. (1.0 mole) of palm oil fatty acids (about 50 percent weight of oleic and 50 palmitic acids) were mixed with 148 gms. (2.0 moles) of isobutyl alcohol in a suitable flask fitted with a Deans-Stark trap, a condenser, stirrer and a thermometer. To this mixture was added 0.6 gm. (0.15 percent based on the weight of the reactants) of methane sulfonic acid and 1.2 gms. (0.30 percent) of 50 percent hypophosphorus acid solution based on the weight of the reactants. The system was raised to the reflux temperature (90°-100° C.) and refluxed at a rapid rate until the theoretical 18 gms. (1.0 mole) of water was collected in the Deans-Stark trap. The system was then cooled to about 50° C. and brought under vacuum (30 mm./Hg) and the temperature increased to distill off the excess alcohol which was recovered. The temperature of the resultant solution was then raised to 100° C.

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at the completion of the distillation, and the ester containing solution was cooled to 50° C. Concentrated aqueous ammonia was added to neutralize the strong acids remaining in the esterification mass, and the product filtered yielding about 300 gms. of isobutyl palmitate-oleate which was recovered as a yellow liquid with a color of 34 (percent transmission, Lumetron, blue filter), or Gardner 5.

## EXAMPLE VI

275 gms. (1.0 mole) of hydrogenated tallow fatty acids (about 30 weight percent palmitic and 70 percent stearic acids) and 148 gms. (2.0 moles) of isobutyl alcohol were mixed in a suitable flask fitted with a Deans-Stark trap, a condenser, a stirrer and a thermometer. To this mixture was added 0.6 gm. (0.15 percent based on the weight of the reactants) of methane sulfonic acid and 1.2 gms. (0.30 percent) of 50 percent hypophosphorus acid solution. The system was then raised to the reflux temperature (90°-100° C.) and refluxed until the theoretical 18 gms. (1.0 mole) of water had been collected in the Deans-Stark trap. The system was then cooled to about 50° C. and brought under vacuum (30 mm./Hg) wherein the temperature was then again raised to distill the excess alcohol which was recovered for re-use. After completion of the distillation, the ester-containing solution was cooled to 50° C. To this cooled solution, concentrated aqueous ammonia was added to neutralize the strong acids remaining in the esterification mass, and the resultant product was filtered to yield about 300 gms. of isobutyl stearate-palmitate. The color was 68 (percent transmission, Lumetron, blue filter), or Gardner 3.

Colors for the above examples and the following tables were determined by comparison against the Gardner 1933 standards and on a Photovolt Lumetron Colorimeter using blue filters. A Lumetron value of 100 (percent transmission, blue filter) or Gardner zero would indicate a colorless liquid (distilled water), while a Lumetron value of zero (percent transmission) would represent a dark colored material equivalent to a Gardner 8. Hence, as a liquid becomes colorless the Lumetron reading approaches 100 percent transmission and the equivalent Gardner value approaches zero.

In order to determine the effect of hypophosphorus acid on the final color of an ester, esterifications were run with and without hypophosphorus acid. The reaction conditions for each specific ester were identical, the only variable being the presence or absence of hypophosphorus acid. The results are shown in the following table:

Table I

Fatty Acid Ester	Conditions of Reaction According to Example—	Percent Hypophosphorus, Acid Added <sup>2</sup>	Lumetron Color (blue filter) to Esterification, Percent Transmission	Gardner
Polyethylene Glycol 400 Di-Lleato.....	1	0.07	63	3
Do.....	1	None	28	5-6
Polyethylene Glycol 600 Mono-Oleate.....	2	0.1	70	2
Do.....	2	None	28	5
Isobutyl Palmitate-Oleate <sup>1</sup> .....	5	0.15	34	5
Do <sup>1</sup> .....	5	None	10	5
Isobutyl Stearate-Palmitate.....	6	0.15	68	2-3
Do.....	6	None	42	4-5

<sup>1</sup> Fatty acid used as a starting material was dark colored.

<sup>2</sup> Based on weight of reactants.

It can thus be seen that when hypophosphorus acid is present during the esterification reaction, the color of the resulting esters were vastly superior to the color of the esters which were prepared in the absence of hypophosphorus acid.

Esterifications were carried out with oleic acid which had been distilled with hypophosphorus acid prior to the

reaction in order to determine the effect of this treatment on the color of a fatty acid ester made with hypophosphorus acid. This treated oleic acid was divided in two equal parts. One part was esterified using hypophosphorus acid as the color inhibiting agent, and the other part esterified in the absence of hypophosphorus acid. Also, esterifications were carried out with oleic acid which was distilled in the absence of hypophosphorus acid. These esterification reactions were carried out according to the procedure of Example I. The results are shown in the following table:

Table II

Oleic Acid Treatment	Esterification with 0.2% p-toluene sulfonic acid	Color of Polyethylene Glycol 400 Ester Lumetron (blue filter), percent	Gardner
Distilled with 0.5% Hypophosphorus Acid.	0.2% hypophosphorus acid added.	170	2
Do.....	No hypophosphorus acid added.	28	5
Distilled without Hypophosphorus Acid.	0.2% hypophosphorus acid added.	89	1
Do.....	No hypophosphorus acid added.	45	4

<sup>1</sup> Distillation was partly carried out using an air stream, but because of the spontaneous combustion of phosphine, nitrogen was used for the remainder of the distillation.

Table II clearly demonstrates that regardless of the prior treatment given to the fatty acids, viz. distillation, or distillation plus the treatment of the fatty acids, with hypophosphorus acid, a discolored ester nevertheless is obtained.

It is therefore apparent that the color of an ester can be improved and/or stabilized by the addition of hypophosphorus acid to the esterification system.

The invention being thus described, it will be obvious that the same may be varied in many ways such as modifications in temperatures and treating conditions. Such variations are not to be regarded as a departure from the essence of the invention and all such modifications are intended to be included within the scope of the following claims.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In the process of esterifying fatty acids with alcohols, the steps which consist essentially of adding from 0.05 to 2.00 percent of hypophosphorus acid based on weight of the fatty acid and the alcohol, to a mixture of at least one fatty acid, at least one member of the group consisting of monohydric and polyhydric aliphatic alcohols having the hydroxyl substituent as the sole reactive substituent and containing from one to about 20 carbon atoms, and an esterification catalyst, esterifying this mixture, neutralizing the acid material contained in the resultant product with a base, and recovering a substantially color-free ester.

2. The process of claim 1, wherein the base is selected from the group consisting of alkali metal and alkaline earth hydroxides, carbonates, bicarbonates and oxides, and organic amine bases.

3. In a process of esterifying fatty acids with alcohols,

the steps consisting essentially of adding from about 0.05 to 2.00 percent of hypophosphorus acid based on the weight of the fatty acid and the alcohol to a mixture containing a fatty acid, a catalyst, and an alcohol selected from the group consisting of monohydric and polyhydric aliphatic alcohols having the hydroxyl substituent as the sole reactive substituent and containing from one to about 20 carbon atoms, heating the mixture for a period of about two to three hours wherein water of reaction is formed, distilling off the resultant water of reaction, neutralizing the formed acid material contained in the resultant product with a base, and recovering a substantially color-free ester.

4. The process of claim 3, wherein the base is selected from the group consisting of alkali metal and alkaline earth hydroxides, carbonates, bicarbonates and oxides, and organic amine bases.

5. The process of claim 3, wherein the alcohol is butyl alcohol.

6. The process of claim 3, wherein the alcohol is octyl alcohol.

7. The process of claim 3, wherein the alcohol is glycerine.

8. In a process of esterifying fatty acids with short chain aliphatic alcohols, the steps consisting essentially of adding from about 0.05 to 2.00 percent of a 50 percent hypophosphorus acid solution based on the weight of the fatty acid and the alcohol to a mixture containing a fatty acid, an esterification acid catalyst, and a short chain aliphatic alcohol having the hydroxyl substituent as the sole reactive substituent, refluxing the mixture in an azeotropic system and azeotropically distilling the formed water of reaction, cooling the resultant solution, and neutralizing the cooled solution with a base and recovering a substantially color-free fatty acid ester.

9. The process of claim 3, wherein the base is selected from the group consisting of alkali metal and alkaline earth hydroxides, carbonates, bicarbonates and oxides, and organic amine bases.

10. In a process of esterifying fatty acids with a polyhydric alcohol, the steps consisting essentially of adding from about 0.05 to 2.00 percent of a 50 percent hypophosphorus acid solution based on the weight of the fatty acid and the alcohol, to a mixture containing a fatty acid, an acid catalyst, and a polyoxyalkylene glycol, subjecting the mixture to a vacuum and raising the temperature to about 130° C. to 140° C. for a period of about two to three hours, distilling the water of reaction as it is being formed, cooling the reaction system under a vacuum to about 50° C., neutralizing with an organic amine base and recovering a substantially color-free fatty acid ester.

11. The process of claim 10, wherein the polyoxyalkylene glycol is a polyoxyethylene glycol.

12. The process of claim 10, wherein the polyoxyalkylene glycol is a polyoxypropylene glycol.

13. The process of claim 10, wherein the organic amine base is triethanolamine.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,071,604

January 1, 1963

Arthur G. Mohan et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 9, for "hyprophosphorus" read -- hypo-phosphorus --; line 19, for "polythydric" read -- polyhydric --; column 6, Table I, first column, line 2 thereof, for "Di-Lleate" read -- Di-Oleate --.

Signed and sealed this 25th day of February 1964.

(SEAL)

Attest:

ERNEST W. SWIDER

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Acting Commissioner of Patents