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FLUORESCEIN AND HALOGENATED FLUORESCEINS DYE ACIDS

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This invention relates to chemistry and more particularly to organic chemistry and has for its object the provision of an improved method of producing organic dye acids known in the art as fluorescein and halogenated fluorescein.

Another object is to provide a method of producing organic dye acids known in the art as fluorescein and halogenated fluorescein in a finely divided amorphous condition.

Still another object is to provide an organic dye acid of one of the group of organic acids known in the art as fluorescein and halogenated flourescein in a finely divided amorphous condition, particularly well suited for use as a tinting agent for greases, oils, waxes, fats, and the like grease-like mediums employed in the cosmetic and other industries.

A further object is to facilitate the incorporation of organic dye acids known in the art as fluorescein and halogenated fluorescein in grease-like mediums.

Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects we have discovered that the addition of an alkali-metal salt of a fatty acid to an aqueous solution of an alkali metal or ammonium salt of an organic dye acid of the group consisting of fluorescein and halogenated fluoresceins, prior to the precipitation of the said organic acid from the said aqueous solution, results in the precipitation of the organic acid in a finely divided amorphous state in association with the fatty acid and that the resultant mixture of organic dye acid and fatty acid blends readily with and disperses readily into the usual grease-like mediums commonly employed in the cosmetic and other arts without requiring much, if any, grinding or mechanical mixing as heretofore found necessary with such organic dye acids.

We have discovered that the amount of the alkali metal fatty acid salt required to obtain this new result may be varied widely without essential departure from the present invention from a minimum amount approximating 1% (by weight) of the organic dye acid up to 50% (by weight), but that for most purposes from about 5% to 15% (by weight) and more specifically, about 10% (by weight), appears to be the most practical for reasons as will hereinafter be apparent.

Heretofore in the art, organic dye acids of the group known in the art as fluorescein and halogenated fluoresceins have been widely used as tinting agents for the various greasy compositions made for the cosmetic trade, as an example, for lipstick compositions. The usual practice followed in forming the organic dye acids is to acidify an aqueous solution of the alkali metal or ammonium salt of the acid with a strong acid under conditions favorable to the formation and precipitation of a finely crystalline organic dye acid precipitate. Organic dye acids formed in this manner are hard crystalline bodies and, no matter how finely crystalline the particle size may be, must subsequently be crushed to a particle size facilitating the uniform dispersion of the same throughout the grease-like mediums into which they are incorporated. This crushing operation is most generally conducted during the operation of incorporating the crystalline organic dye acid in one or more of the ingredients of the grease-like medium for the reason that considerable difficulty is also experienced in wetting the surface of the crystalline particles with the oils, waxes, fats and fatty acids commonly employed in such grease-like mediums.

In contrast with this, the finely divided amorphous material of the present invention consisting of a mixture of finely divided organic dye acid in its amorphous state intimately admixed with a fatty acid, blends perfectly and readily with all of the oils, waxes, fats and fatty acids commonly employed as constituents of the grease-like mediums employed in the cosmetic art with a minimum of mechanical agitation to obtain a uniform dispersion of the same throughout the said medium and with substantially no grinding required to obtain the desired ultimate fine particle size of the dye acid therein.

As a specific embodiment of the present invention, but not as a limitation thereof, we will describe the practice of the present invention insofar as it has been developed for the production of finely divided amorphous tetrabromofluorescein ($C_{20}H_8O_5Br_4$) and an intimate admixture consisting of finely divided amorphous tetrabromofluorescein and stearic acid, which mixture is particularly suitable for use as a tinting agent in the specific grease-like materials commonly employed in the forming of lipsticks.

To a solution of an alkali metal salt of tetrabromo-fluorescein, containing approximately 10 grams per liter of the said salt, for example, the sodium salt of tetrabromofluorescein, about one (1) gram of the sodium salt of stearic acid is added and the resulting solution is acidified with hydrochloric acid to slight excess to insure sub-

stantially complete precipitation of the dye and fatty acids present in the solution.

Preferably, the precipitation of the organic acids (halogenated fluorescein and stearic acid) is accomplished at room temperatures and with vigorous agitation during the acid addition and the acid additions are made to the solution at a relatively slow rate to promote the formation of a relatively small particle sized amorphous precipitate of the said organic dye acid.

Following precipitation of the organic acids (tetrabromofluorescein and stearic) the solution may be heated to facilitate the washing and filtering operations. Preferably, however, the solution temperature is maintained substantially below the melting point of stearic acid (69.4° C.) to prevent agglomeration of the precipitate and/or clogging of the filter. After drying the filter cake will ordinarily crumble to a soft fine powder where the processing temperatures have not been sufficiently high or sufficiently prolonged at a high temperature to produce agglomeration.

The amorphous dye acid may be recovered from the dry mixture of dye acid and stearic acid by selectively dissolving out the stearic acid as by suspending the mixture in an organic solvent such as petroleum ether, solvent naptha, and other organic solvents, in which the fatty acid is soluble, but the dye acid insoluble or only slightly soluble.

Where the dye acid, however, is to be incorporated in the grease-like material forming the base of a cosmetic preparation such as a lipstick, the stearic acid content of the mixture is not removed and the mixture of dye acid and fatty acid is added directly to the grease-like material in the relative amounts desired to impart thereto the desired color intensity. The stearic acid content of the mixture which apparently superficially covers the surface of each particle of the dye acid greatly facilitates the incorporation of the dye acid in the grease-like liquified medium and the extreme softness of the dye acid in combination with its small particle size greatly facilitates the dispersion of the dye acid uniformly throughout the medium with the minimum of mechanical agitation and grinding forces.

In place of stearic acid in the above specific embodiment we may employ any of the other fatty acids in the well known series of fatty acids having from 11 to 19 carbon atoms attached to the COOH group, such as, for example:

Lauric acid—$C_{11}H_{23}\cdot COOH$
Myristic acid—$C_{13}H_{27}\cdot COOH$
Palmitic acid—$C_{15}H_{31}\cdot COOH$
Stearic acid—$C_{17}H_{35}\cdot COOH$
Oleic acid—$C_{17}H_{33}\cdot COOH$
Arachidic acid—$C_{19}H_{39}\cdot COOH$

Various mixtures of these acids as may be contained in saponified naturally occurring fats and oils such as palm oil, tallow, cottonseed oil, cocoanut oil, peanut oil, and the like, are equally as effective as substitutes for the alkali metal salt of stearic acid in the above specific embodiment, such substitution requiring only the regulation of the solution temperature during the precipitation of the dye and fatty acids with respect to the physical properties of the precipitated fatty acid to avoid undesirable agglomeration of the precipitated acids and an adjustment of the relative quantity of the fatty acid to the dye acid to compensate for the greater or lesser dispersion and covering properties of the fatty acid employed as compared with the stearic acid of the specific improvement given. Whereas stearic acid is normally a solid at atmospheric temperatures and oleic acid is normally a liquid at atmospheric temperatures, the effect of the two acids on the structure of the dye acid precipitated simultaneously therewith in accordance with the present invention appears substantially identical and to be the result of adsorption of the fatty acid by the dye acid.

However, excellent dispersion properties are obtained with a stearic acid content as low as 1% in the precipitated dye acid and for some purposes, particularly where a high stearic acid content in the grease-like base is immaterial or even desirable, as high as 50% stearic acid content may be employed without deleterious effect upon the particle size or the amorphous character of the dye acid precipitate. For most purposes, however, a mixture consisting of approximately 10% stearic acid and 90% dye acid appears to be the most desirable and the most easily prepared and handled on any large commercial scale.

It is believed equally as well apparent to any one skilled in the art that in place of the tetraboromofluorescein of the specific embodiment, any other dye acid of the group including fluorescein and halogenated fluoresceins may be substituted without departure from the present invention. Each of the members of this group are well recognized as being chemically equivalent to the tetrabromofluorescein in the chemical reactions involved in this invention. Stearic acid additions thereto in the manner hereinabove described similarly functions to inhibit the formation of hard crystalline bodies and to promote the formation of soft amorphous particles during the precipitation of the dye acid from aqueous solutions of its alkali metal or ammonium salt on acidifying the solution with an acid, such as HCl, and any of the other fatty acids of the group mentioned will react identically to stearic acid when substituted therefor in part or in whole.

Having hereinabove described the present invention generically and specifically, it is believed apparent that the same may be widely varied without essential departure therefrom and all such modifications and departures are contemplated as may fall within the scope of the following claims.

What we claim is:

1. The method of producing a dye acid of the group consisting of fluorescein and halogenated fluoresceins in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and a long chain fatty acid from an aqueous solution containing the water soluble salts of the said dye and fatty acids.

2. The method of producing a dye acid of the group consisting of fluorescein and halogenated fluoresceins in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and a long chain fatty acid of the group containing at least 11 carbon atoms in the carbon chain attached to the COOH group thereof from an aqueous solution containing the water soluble salts of the said dye and fatty acids.

3. The method of producing a dye acid of the group consisting of fluorescein and halogenated fluoresceins in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and stearic acid from an

aqueous solution containing the water soluble salts of the said dye and fatty acids.

4. The method of producing tetrabromofluorescein in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and a long chain fatty acid from an aqueous solution containing the water soluble salts of the said dye and fatty acids.

5. The method of producing tetrabromofluorescein in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and a long chain fatty acid from an aqueous solution containing the water soluble salts of the said dye and fatty acids, said fatty acid being one of the group of fatty acids containing at least 11 carbon atoms in the carbon chain attached to the COOH group thereof.

6. The method of producing tetrabromofluorescein in a soft amorphous-like form, which comprises simultaneously precipitating the dye acid and stearic acid from an aqueous solution containing the water soluble salts of the said dye and fatty acids.

7. The method of producing a dye acid of the group consisting of fluorescein and halogenated fluoresceins which comprises forming an aqueous solution containing about 10 grams per liter of a water soluble alkali metal salt of said dye acid and about 1 gram per liter of a water soluble alkali salt of a fatty acid of the group of fatty acids having at least 11 carbons in the carbon chain attached to its COOH group, acidifying the solution with a mineral acid to precipitate the dye acid and fatty acid, and separating the precipitated acids from the solution.

8. The method of claim 7, wherein during the mineral acid addition to the solution, the solution in vigorously agitated to inhibit the formation of large particle sized precipitated dye acids.

9. The method of claim 7, wherein the said dye acid comprises tetrabromofluorescein, the said fatty acid comprises stearic acid, the said solution is vigorously agitated during the mineral acid addition to inhibit the formation of a large particle sized dye acid precipitate and the temperature of the said solution is maintained below the melting point of stearic acid.

10. The method of producing a dye acid of the group consisting of fluorescein and halogenated fluoresceins in a relatively soft amorphous condition which comprises precipitating said dye acid from an aqueous solution of its water soluble alkali metal salt containing in addition to the said dye acid salt a proportion ranging from 1% to 50% (by weight of dye acid) of a water soluble alkali metal salt of a fatty acid containing at least 11 carbon atoms in the carbon chain attached to its COOH group, maintaining during the precipitation of said dye acid a solution temperature approximating atmospheric temperatures.

11. The method of claim 10, wherein the specific method of precipitating said dye acid is regulated such as to produce a relatively small particle sized dye acid precipitate.

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