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2,940,902

PROCESS FOR THE PRODUCTION OF COSMETIC CREAMS AND THICKENING AGENTS THEREFOR

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8 Claims. (Cl. 167—87)

This invention relates to a process of preparing clear, transparent and easily removable aqueous jellies to serve as vehicles for cosmetic agents such as those employed, for example for hair dyeing, tinting, bleaching, waving and other types of treatment.

According to the invention, the above process comprises combining into a salt-like compound the hydrophobic cation of a higher cation-active organic base selected from the group consisting of ammonium and sulfonium compounds with the hydrophobic anion of a higher anion-active organic acid and gradually adding water to said salt-like compound until a desired consistency or gel is obtained. This application is a continuation-in-part of my abandoned application, Ser. No. 327,442, filed December 22, 1952.

The present invention relates also to means for the treatment of hair, and more particularly to means for the dyeing and permanent waving of hair.

It is preferable to employ the above said means in the form of creams and the like, because it is advantageous to be able to localize the action of the reagents and to avoid an action on the skin of the person being treated.

In the dyeing of hair, there are normally employed supports such as, e.g., fatty alcohols, stearates of glycol or glycerol, polyoxyethylene derivatives, methyl cellulose, carboxymethyl cellulose and the like.

These cream bases have a number of disadvantages such as, e.g., the tenacity with which they adhere to the hair, whereby the rinsing is made a complicated operation, and the opacity of the creams.

In the permanent waving of hair, there is the additional difficulty that the winding up of the hair on curlers is made practically impossible if the treating product must contain too much of the base to form a cream, because the hair is then made too slippery for being handled. Usually the means for permanent waving are therefore merely thickened or emulsion-like solutions, but not creams.

It is an important object of the present invention to provide means to overcome the described difficulties.

It is another object of the present invention to provide methods and means allowing the preparation of hair-dyeing creams which are transparent, easy to apply and easy to remove from the hair.

It is a further object of the invention to provide methods and means for preparing a permanent waving cream not subject to the aforementioned drawbacks.

It is a further object of the invention to provide means for the described purpose, which are inexpensive to manufacture and at the same time exert a useful influence on the hair being treated.

The invention accordingly consists of the compositions and steps which will be exemplified in the compounds and processes next described, the scope of the invention being determined by the appended claims.

I have found that the described deficiencies of known products can be overcome if the aforesaid creams are prepared from new thickening bases which until now have

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not been proposed for hair-treating products. These new bases are salt-like compositions of high molecular organic bases and high molecular organic acids in substantially equi-molecular amounts.

These organic high molecular bases derive from a basic central atom, such as nitrogen, sulfur etc.; in other words they belong to the class of so-called onium-compounds. They contain at least one organic radical of 8 or more carbon atoms and one nitrogen atom or the like, with a basic reaction, and may contain other radicals of lower molecular weight.

These products are often named higher cation-active products because of their ability to give foaming solutions at acid pH-values, the cation being the part of the molecule which carries the hydrophobic radical.

The organic high molecular acids mentioned above contain at least one organic radical of 8 or more carbon atoms and at least one group with acid reaction as for instance the sulfonic acid radical, the carboxyl radical, the radical of phosphoric acid, etc. These products are often called higher anion-active products because in this case the anion is the part of the molecule which bears the hydrophobic group. The reaction products of these two components may be prepared by melting together the free base and the free acid or, they may be prepared by double reaction of their salts with low molecular bases and acids and contingently eliminating the by-products.

They are wax-like substances that can be used as supports for cosmetic creams with the following advantages:

(1) They yield transparent creams and thereby allow complete observation and control of the action on the substrate as for instance the human hair.

(2) They allow the making of such creams or gels with only a few percent of the thickening base which makes the products very inexpensive.

(3) If higher percentages are employed, the creams can be diluted with water or aqueous solutions (e.g. H_2O_2) without any loss of viscosity.

(4) They allow the preparation of cold-wave-creams which in view of the low percentage of base are not slippery.

(5) On the other hand any other high molecular anion or cation than that of the base liquefies the cream almost instantaneously which makes it possible to rinse the treating cream very easily off the hair.

(6) If the thickening bases are dissolved together with the treating composition in organic hydrophilic solvents such as ethyl alcohol, isopropyl alcohol, butanol, glycols, glycol monoalkyl ethers etc., it is possible to prepare thin liquids which thicken instantaneously to a cream if there is added water or an aqueous solution.

As already known, cation-active substances consist of high molecular weight organic compounds containing one or more basic groupings derived from phosphorus, sulphur, oxygen or more particularly quaternary or non-quaternary nitrogen. Among the better known of these compounds there may be mentioned the "Sapamines" of Ciba Ltd, the "Soromines" of the B.A.S.F. and the "Velan" of I.C.I. Ltd. Compounds of this class are known as "invert soaps" and they are applied in the form of salts derived from acids of low molecular weight such as methyl sulphuric acid, acetic acid and hydrochloric acid in order to increase their solubility and to bring into effect their cation-active properties.

More particularly, some of the above "Sapamines" are: chlorhydrate of oleyl-aminodiethyl-amine, chlorhydrate of oleyl-benzylaminoethylenediethylamine, methyl-sulfate of monostearyl-ethylene-diaminetriethylammonium and methylsulfate of diethylaminoethyloleamide asymmetric. Some of the "Soromines" are: stearic ester of dibutylaminoethanol, monostearic ester of triethanol-

The properties described above make it possible to obtain entirely new preparations. Thus, for example, a concentrated solution (about 10 to 20%) in organic solvent, upon addition to an aqueous solution, for example

Two parts by weight of this product are dissolved in 15 parts by volume of ethyl alcohol; to this solution is added 3 parts by volume of a bi-molar acetic acid solution and 30 parts by volume of water. It results a thick

cream of acid reaction to which there may be added dyes to prepare a hair rinse.

EXAMPLE 6

In the same manner as in the preceding example there is prepared a reaction product of equimolecular tities of the above cited cation and an anion-active product of the formula $C_{12}H_{25}O.CH_2.CH_2.OCH_2.CH_2.SO_3Na$. To precipitate the reaction product, it is preferable to add a salt, e.g. ammonium sulfate.

Three parts by weight of the anion-cation-product are dissolved in 5 parts by volume of ethyl alcohol and mixed with 22 parts of water. It results a jelly-like cream which can be alkalinized; e.g. with ammonia, or acidified e.g. with acetic acid or lactic acid. It may be taken as a base for hair-creams or for alkaline hair-bleaching creams, the latter for instance by diluting the ethanolic solution with aqueous hydrogen peroxide instead of water.

It is also possible to prepare a cream from the described base simply by heating the anion-cation product with water and adding the other ingredients after cooling.

EXAMPLE 7

In the same way as in the preceding example there can be prepared a base with similar properties by reacting cetyltrimethylammoniumbromide with ammonium dodecylsulfate.

The wax-like reaction product gives a beautiful cream in mixtures of alcohol and water. It may be taken as a base for a number of cosmetic treating products, such as hair dyes, vanishing creams and the like.

EXAMPLE 8

30 parts by weight of dihydroxydiethelenetriaminedistearylamide and 12 parts of myristic acid are melted together while stirring. On cooling, there results a soft wax-like product.

3 parts by weight of this product are heated with 52 parts of water and added 5 parts by volume of a 25% ammonium hydroxide solution after cooling. A beautiful jelly-like cream is obtained. It may be used as a base for hair-dyeing-creams, hair-bleaching creams, permanent waving creams and the like.

EXAMPLE 9

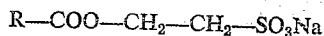
Thickener

In place of the waxy product, described in Example 1, there can be employed the product prepared as follows:

305 parts of sodium oleate dissolved in two thousand parts of distilled water are treated with 855 parts of a 40% solution of lauryldimethylsulfonium methosulfate without shaking. The anion-cation complex (lauryldimethylsulfonium oleate) precipitates in dispersed form which is difficult to separate by centrifuging. The dispersion is saturated with sodium chloride and the complex extracted with amyl alcohol. The extract is distilled under reduced pressure leaving a residue of waxy consistency.

EXAMPLE 10

An aqueous solution of a compound of the following formula



wherein R represents a saturated aliphatic chain of 11 to 13 carbon atoms was mixed with an aqueous solution containing an equimolecular amount of dodecyltrimethylbenzylammonium chloride. The anion-cation compound which precipitated was separated by filtration and dried. A creamy gel could be prepared by dissolving 3 parts (by weight) of the reaction product in 5 parts (by volume) of 1,4-butanediol and adding thereto a mixture of 5 parts (by volume) of ammonia (25% NH_3) and of 20 parts of water. This cream may be used as a base for hair-dyeing mixtures containing so called "oxidation dyes."

In lieu of butanediol, other hydrophilic solvents, such as glycerol, may be used.

EXAMPLE 11

Removal of a hair-treating product

An interesting feature of the aqueous jellies prepared in accordance with the invention relies on their easy removal by application of an excess of any suitable ionic and water-soluble surface active agent in aqueous solution, for instance an anionic or a cationic shampoo. This advantage is evidenced by the following tests.

One volume of a ten percent isopropanolic solution of the thickening agent described in Example 1 was mixed with three volumes of water. The resulting product is a cream having a viscosity of 1240 centipoises at 20° C. as measured with a Höppler viscometer. By adding to 100 cc. of said cream 0.4 g. of ammonium dodecylsulfate dissolved in 2 cc. of water, the structure of the cream is altered and the viscosity drops to 0.3 centipoises, i.e. a value hardly higher than that of plain water.

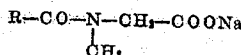
EXAMPLE 12

One part of a 0.2 molar aqueous solution of lauryldimethylsulfonium methosulfate is added, under gentle stirring, to one part of a 0.2 molar aqueous solution of sodium laurylsulfate (commercial grade) of an apparent, average molecular weight of 333. A flaky precipitate is formed, which is the anion-cation complex, i.e., the lauryldimethylsulfonium laurylsulfate. This precipitate is dissolved in one part of isopropyl alcohol.

The isopropanolic solution, when poured in water, yields a viscous, translucent syrup of a jelly-like consistency.

EXAMPLE 13

Equimolecular amounts of cetyltrimethylammonium bromide and of a sarconsinate of the general formula:



wherein R represents a saturated aliphatic chain of 11 to 13 carbon atoms (such as the product known as "Medialan KA") are mixed together in aqueous solution. A stiff jelly is obtained which can be used directly as a thickener for alkaline solutions of a high salt content, such as permanent hair-waving solutions.

For instance, 15 parts of crystalline sodium sulfite are dissolved in 85 parts of the above-mentioned jelly, which contains 5 percent by weight of the anion-cation complex. 30 parts by volume of a bi-molar ammonium hydroxide solution are then added. A cream is obtained which can be used for permanent hair waving.

In an analogous manner, ammonium thioglycollate can be used in lieu of sodium sulfite without noticeably altering the initial consistency.

EXAMPLE 14

Equimolecular amounts of cetyltrimethylammonium bromide and of a taurate of the formula:



wherein R represents a saturated aliphatic chain of 11 to 13 carbon atoms, are mixed together in aqueous medium. Upon gentle warming, two layers separate. The supernatant layer is decanted. It contains the anion-cation complex and 71.5% water. Upon cooling, it sets to a firm jelly which can be further diluted with water or with organic hydrophilic solvents.

For instance, a transparent gel is obtained by diluting 7.5 parts of the decanted layer with 25 parts of glycerol, 5 parts of water and 3 parts of ammonia ($d=0.910$).

$$\begin{array}{l} \text{C}_{17}\text{H}_{35}-\text{CO}-\text{NH}-\text{CH}_2-\text{CHOH} \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ \quad \quad \quad \text{N}-\text{OC}-\text{CH}_3 \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \text{C}_{17}\text{H}_{35}-\text{CO}-\text{NH}-\text{CH}_2-\text{CHOH} \end{array}$$

EXAMPLE 16

$$\text{CH}_3-(\text{CH}_2)_4-\text{COO}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$$
$$\text{R}-(\text{OCH}_2\text{CH}_2)_n-\text{OSO}_2-\text{S}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{OOC}-(\text{CH}_2)_r-\text{CH}_3$$

What is claimed is:

2. A process of preparing clear, transparent and easily removable aqueous jellies to serve as vehicles for cosmetic

2. A process of preparing clear, transparent and easily removable aqueous jellies to serve as vehicles for cosmetic

8. A method of preparing cosmetic jellies which consists essentially of dissolving into an organic hydrophilic solvent a cosmetic agent and a salt-like compound obtained from the combination of the hydrophobic cation of a higher cation-active organic base selected from the group consisting of ammonium and sulfonium compounds with the hydrophobic anion of a higher anion-active organic acid and adding water to the resulting solution to obtain a predetermined consistency.

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