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DEXTRAN COMPOUND FATTY ACID ESTER LIPSTICK

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This invention relates to cosmetic preparations. More specifically, the invention relates to cosmetic sticks or pencils, such as lipsticks, perfume sticks, eyebrow pencils, etc., and to creams, shampoos, and such other cosmetic preparations as include a wax-like base.

To be entirely satisfactory lipsticks and cosmetic sticks generally must be resistant to summer heat and winter cold while remaining of essentially the same hardness and retaining essentially the same rubbing quality through seasonal temperature changes, and, more especially in the case of lipsticks, they must be resistant to removal by aqueous liquids, induce no allergic reactions and exhibit no irritating effects on the sensitive skin of the lips.

Conventionally, cosmetic sticks are made of mixtures of waxes, fats, emollients, and oils which form the base of the preparations. For lipsticks, specific coloring matter is added to the basic mixture; for perfume sticks essential perfume oils are added. For other special uses, the appropriate ingredients are incorporated with the base mixture.

It is well known that considerable research has been performed in an effort to compound a non-irritating, liquid-resistant base, binder or carrier for the coloring matter of lipsticks and having adequate staying power in all weather. It is also known that the conventional lipsticks composed of oil-soluble dyes distributed in a natural wax containing castor oil as solvent for the coloring matter are not satisfactory.

When applied, such lipsticks leave a layer of a colored mixture of the wax and oil and the color effect from their application lasts only about as long as the fatty layer remains. Since such bases are readily washed off or removed by fluids or foods as well as mechanically by moving the lips or touching them, the coloring effect soon disappears. Such products also have the disadvantage of being readily smeared and becoming unsightly. To overcome this difficulty it has been proposed to incorporate in a natural wax-oil base a water-soluble coloring substance or dye which actually stains the lips. Such staining agents are included in so-called "indelible" lipsticks. However, the indelible lipsticks are not generally satisfactory. Their use often leads to excessive dryness and cracking or chapping of the lips which is both uncomfortable and unattractive.

It is a general object of this invention to provide new cosmetic compositions.

Another object is to provide lipstick compositions including a carrier or base which is water-repellent, firmly adherent to the lips, non-irritating, and which does not result in drying or cracking.

A specific object is to provide an improved long-lasting lipstick comprising coloring matter which is not a stain, incorporated in a water-repellent, firmly adherent, non-smearing, harmless base or carrier.

These and other objects of the invention are accomplished by new compositions comprising the cosmetic materials distributed in a base comprising or consisting of an ester of a dextran with a fatty acid containing from 8 to 18 carbon atoms and having an average D. S. (degree of substitution or the average number of fatty acid radicals per anhydroglucopyranosidic unit of the dextran) of from less than 1.0 to 3.0.

The dextrans are high molecular weight, branched polysaccharides containing anhydroglucopyranosidic units linked together by molecular structural repeating linkages some of which are alpha-1,6 linkages, others are non-alpha-1,6 linkages and at least 50% of these linkages being, apparently, alpha-1,6 linkages. The dextrans vary with respect to their molecular structural repeating alpha-1,6 to non-alpha-1,6 linkages ratios, the extent of branching (the distribution and length of side groups or chains), their molecular weight, and their sensitivity to moisture.

The pure or substantially pure dextrans are bland, non-toxic, non-irritating substances which are more or less hydrophilic. In accordance with the present invention it is found that while esters of the dextran with the fatty acids of from 8 to 18 carbon atoms differ from the parent dextrans in being more or less water-resistant, they are like the dextrans in being bland, non-irritating harmless substances ideally adapted to use as the base for various types of cosmetic preparations.

The higher fatty acid radicals may be introduced into the dextran molecule in any suitable way, as by the methods disclosed in the pending application of L. J. Novak and J. T. Tyree, Serial No. 351,743, filed April 28, 1953. Thus, the selected dextran may be reacted with an esterifying derivative of the higher fatty acid, and preferably a halide such as the chloride thereof, in the presence of an acid acceptor or binding agent such as an organic base, as for instance a tertiary heterocyclic amine of the type of quinoline, pyridine, N-methylmorpholine, etc. and in the presence of a substance in which the reaction product is at least partially solvated, that is dissolved or swollen, as it is formed during the reaction, which results in the reaction mass being maintained in a highly swollen or dissolved state and thus insures substantially uniform, homogeneous reaction between the dextran and the esterifying agent. Substances which dissolve or swell the ester as it is formed are, for example, xylene, toluene, dioxane, etc. In general, the reaction is carried out at temperatures between 100° C. and 155° C. for time periods varying inversely with the temperature between a half hour and three hours, both the temperature and the reaction time depending on the boiling point of the mixture of acid acceptor and solvating agent used. Thus, if a mixture of quinoline and xylene is used, the reaction may be effected by heating the mass at from 150° C. to 155° C. for from one-half hour to an hour, whereas when a mixture of pyridine and toluene having a relatively low boiling point is employed the reaction is preferably run at temperatures of 100° C. to 115° C., for from one to three hours. The dextran may be recovered from the crude reaction mix, in which it is at least partially dissolved, by washing the mixture with water to remove the hydrochloride of the organic base, removing the aqueous layer, adding a solvent for the ester to the residual mass, and pouring the solution thus obtained into a non-solvent for the ester, such as a lower aliphatic alcohol, e. g., methanol, ethanol, isopropanol, etc., and filtering the ester, which may be further purified by re-precipitation, and dried.

Introduction of the high fatty acid radicals into the dextran molecule may be effected, also, by reacting the dextran with the selected acid, in the presence of an "impeller" which may be a monohalogenated monobasic organic acid anhydride and an esterification catalyst such as magnesium perchlorate at temperatures at which the reaction mixture remains in the liquid state and, depending on the acid and dextran used, generally in the range between 50° C. and 100° C. and for a time varying in-

versely with the temperature between one-half hour and two hours. The ester is isolated from the crude reaction mass by cooling the mass, dissolving it in a solvent therefor, and precipitating it into a non-solvent for the ester in which the chloracetic acid (formed by addition of by-product water to the anhydride "impeller") remains in solution, and filtering to remove the ester. The latter may be dried in any suitable manner.

The higher fatty acids which may be used in the free acid condition or in the form of their chlorides are those containing from 8 to 18 carbon atoms and including caprylic, pelargonic, capric, undecyclic, lauric, tridecyclic, myristic, pentadecyclic, palmitic, margaric and stearic acids and the corresponding chlorides. The esters used in the cosmetic preparations of the invention may be mixed esters such as mixed dextran stearate-palmitate resulting from the reaction of a dextran with commercial stearic acid, known to be a mixture of stearic and palmitic acids.

These esters are water-resistant to a degree depending on the kind and number of acid radicals combined therein. The D. S. may be from less than 1.0 to about 3.0, resulting from use of the esterifying agent in amounts between less than 1.0, say 0.5, to 10.0 parts thereof per part of dextran.

The ester may be selected for the particular type of cosmetic of which it is to comprise the base, alone or in admixture with other adjuvants including inert fillers and conventional waxes and oils. Thus, those esters having a D. S. from about 2.5 to 3.0 and derived from fatty acids containing from 14 to 18 carbon atoms are water-repellent substances of wax-like consistency. These water-repellent esters are particularly suited to use as the base of compositions for use as cheek rouge or molding into lipsticks. They are remarkably adherent to the skin. For instance if a film of a dextran palmitate or of a dextran stearate containing an average of 2.9 palmitoyl or stearoyl radicals per anhydroglucopyranosidic unit forms on the hands during handling of dispersions or solutions of those esters, the film is not removed by vigorous scrubbing with soap and water. Used as the base or binder for cosmetic preparations, these water-repellent, wax-like dextran fatty acid esters, yield products which have excellent hardness at normal temperature extremes, rub off readily when applied to the skin, and exhibit good staying power on the skin. These esters may also be used as the base for so-called "solid" perfumes such as perfume sticks comprising essential perfume oils.

On the other hand, the dextran esters of lower D. S., i. e., those containing an average of from less than 1.0 up to about 2.0 of the fatty acid radicals per anhydroglucopyranosidic unit, are preferred for use as base component for other types of cosmetic products such as creams, shampoos, and similar products and in which the dextran ester functions as a base or binder and may also serve as a suspending agent.

The low-substituted esters are more resistant to water than the parent dextrans, their water-sensitivity being a function of the number of free hydroxyl groups present in the ester. Since this in controllable by adjustment of the conditions for producing the esters, including the relative proportions of dextran and esterifying agent, the ester may be selected for the particular use for which it is intended. The more water-sensitive esters are very suitable for use when a gradual and regulated release of volatile constituents of the composition is desired. An example is perfume blocks or sticks comprising essential perfume oils. These oils may be incorporated in a base comprising or consisting of a water-sensitive dextran higher acyl ester having some free hydroxyl groups so that when, in the presence of body moisture, the dextran swells and may gradually dissolve, the oils are released at a gradual, more or less regulated rate.

Whatever the precise form of the cosmetic, whether it is a lipstick, or a cream, paste, etc. the dextran fatty acid ester will usually comprise at least 30%, in most cases, at least 50% of the base. In many instances the base will consist of the dextran ester. However, small amounts of wax such as ozokerite, beeswax, carnauba wax, and spermaceti may be mixed with the ester. The base may also contain, in addition to the dextran ester, small amounts of such substances as cocoa butter, butyl stearate and lanolin. Oil-soluble coloring materials may be dissolved in an oil, such as castor oil, and the solution may be mixed with the base comprising dextran palmitate or the like.

It is also within the scope of the invention to include in the cosmetic preparation a finely divided inert filler, these finely divided filler materials being held together by the dextran ester binder and serving, in the case of sticks or the like, as a structure or body material for imparting additional strength to the stick. The filler also functions as a diluent for the coloring material and assists in effectively dispersing the same through the base. For the structure or body material there may be used such materials as talc, kaolin, clay, bentonite and other similar particulate inerts.

The coloring material may be any of the oil-soluble certified DC colors or lake colors for lipsticks, cheek rouge, etc., and which are known in the art as drug and cosmetic colors. Such colors are preferably dissolved in castor oil and mixed in the dissolved condition with the base. Or compositions may include, as coloring material, a stain, for instance a water-soluble cosmetic dye which is insoluble in waxes or fats and suspended or dispersed in the base composing the dextran palmitate or the like. Compositions according to the invention, including a stain, have the advantage that the stain, when combined with the dextran ester base, shows less tendency to induce chapping or cracking of sensitive skins than they commonly exhibit when applied to the lips or skin in conventional bases comprising natural waxes. The dyes to be used depend on the intensity or shade required. Suitable dyes include ponceau 3R, amaranth, purified eosine y, tartarzine, yellow ochre, etc., or any of the dyes used in "indelible" lipsticks. Various dyes may be used together in selected proportions to give desired shades.

The compositions may take the form of solid or semi-solid cosmetic products, creams, pastes, cream shampoos, deodorants, etc. and may be modified as desired by the addition of oils to give them emollient or lubricating properties. Solid or semi-solid products, e. g., sticks, useful as long-lasting perfumes may be made by incorporating in the base suitable essential perfume oils.

The low-substituted esters having some free hydroxyl groups and more or less sensitivity to water, are, as has been mentioned above, useful as the base substance when release of the active cosmetic at regulated, controlled rate is desirable. Those esters tend to swell and may eventually dissolve in the presence of moisture. Their use is indicated in perfumes, deodorants and the like. In such applications, when the composition comprises a homogeneous mixture of concentrated perfume oils and a partial dextran higher fatty acid ester, as the ester is swollen in contact with the moisture of the skin, the perfume oils combined therewith are released at more or less regulated rate and thus it is possible to prolong the effect thereof. The same is true of homogeneous mixtures of the partial dextran esters and active deodorizing ingredients.

The dextran which is reacted with the higher fatty acid or its chloride to produce the esters to be used as bases or binders in the practice of this invention may be obtained in any suitable way. It may be produced microbiologically, for instance by inoculating a nutrient medium containing sucrose, particular nitrogenous compounds, and certain inorganic salts with an appropriate bacterium such as those of the *Leuconostoc mesenteroides* and *L. dextranicum* types and incubating the culture at the temperature most favorable to the growth of the particular bacterium.

In one method of obtaining a dextran by bacterial ac-

tion, there is first prepared an aqueous nutrient medium which may have the following composition:

	Percent by weight
Sucrose	20
Corn steep liquor	2
Monobasic potassium phosphate	0.5
Manganous sulfate	0.002
Sodium chloride	0.50
Water	Balance

This medium is adjusted to a pH of between about 6.5 and about 7.5, preferably 7.2, and then sterilized. The material is cooled to room temperature and inoculated with a culture of the dextran-producing bacteria, for example, *Leuconostoc mesenteroides* B–512 (Northern Regional Research Laboratory classification) and incubated at 20° to 30° C. (optimum 25° C.) until a maximum yield of dextran has been attained; normally a period of between 12 and 48 hours will be satisfactory for this procedure. The fermented product contains approximately 80–85% of water and is a thick turbid liquid.

Upon completion of the fermentation, which process renders the material somewhat acid, that is, to a pH of 3.5–5.5 (average 4.2), calcium chloride is added to the ferment to bring the pH thereof to about 7.0 to 8.0. This aids in the precipitation of phosphates. Thereafter, acetone or alcohol, which may be a water-miscible aliphatic, such as methyl, ethyl or isopropyl, is added in sufficient quantity to precipitate the dextran and this brings down, with the dextran, occluded and adsorbed bacteria, and nitrogenous and inorganic elements. To occasion complete precipitation of the dextran it may be desirable to allow the mix to stand for a relatively long period, such as about 6 hours. The precipitated dextran may be dried in any suitable manner, for example by drum drying to obtain a flaky product. Thereafter, it may be reduced to powdered condition, if desired.

A purer dextran may be obtained by adding an aliphatic alcohol to the fermented culture at a pH between about 2.5 and 4.5. The precipitate thus obtained may be further purified by again precipitating it with the alcohol. Several precipitations may be performed.

Such a "native" high molecular weight dextran (the molecular weight is calculated to be in the millions) may be used in practicing this invention. In the alternative, and for some purposes, preferably, a dextran having, initially, a high molecular weight is hydrolyzed to a product of lower molecular weight for esterification with the higher fatty acid or esterifying derivative thereof. For instance, the "native" dextran obtained as described above may be hydrolyzed to a product having a lower molecular weight or lower average molecular weight, for instance and average molecular weight in the range between 20,000 and 200,000 and this hydrolyzed product, if desired or necessary may be fractionated by available methods to obtain a fraction of pre-selected uniform or more nearly uniform molecular weight in the stated range, such as a fraction having a molecular weight or average molecular weight in the range 70,000 to 85,000. The fraction of pre-selected molecular weight may be, if desired, treated by known methods for the removal of pyrogens and coloring materials, prior to the esterification. The dextran used in preparing the higher fatty acid esters may be a so-called "clinical" dextran. In general, the dextran may have a molecular weight between 5,000 and 150×10^6 as determined by light scattering measurements.

The dextran to be esterified may be obtained by inoculating the culture medium with microorganisms bearing the following NRRL classifications: *Leuconostoc mesenteroides* B–119, B–1146, B–1190; or it may be a water-insoluble or substantially water-insoluble dextran obtained by inoculating the nutrient medium with the microorganisms *Leuconostoc mesenteroides* B–742, B–1191, B–1196, B–1208, B–1216, B–1120, B–1144 or B–523, *Streptobacterium dextranicum* B–1254, or *Betabacterium vermiforme* B–1139.

The invention is not limited to esters of dextran produced under any particular set of conditions or using any particular microorganism. The dextran may be produced enzymatically, in the substantial absence of bacteria, by cultivating an appropriate microorganism, such as *Leuconostoc mesenteroides* B–512 to obtain a dextran-producing enzyme, separating the enzyme from the medium in which it is produced, and introducing the enzyme into a medium in which dextran is produced by the action of the enzyme. Also, the dextran may be obtained by bacterial conversion of 1,4 linkages of dextrin to 1,6 linkages of dextran, or in any other suitable manner.

The following formulations, in which the parts are given in percentages by weight, are illustrative of specific embodiments of the invention. The colors used in Formulae I–V are certified DC colors or lake colors for lipsticks and known as drug and cosmetic colors.

(I)	Dextran palmitate derived from clinical dextran; average D. S. 2.9 palmitoyl radical	74.0
	Colors	26.0
(II)	Dextran palmitate as in Formula I	69.5
	Castor Oil	5.5
	Colors	25.0
(III)	Dextran palmitate as in Formula I	52.5
	Lanolin	12.0
	Castor oil	5.5
	Colors	30.0
(IV)	Dextran stearate from clinical dextran; average D. S. 2.9 stearoyl groups	65.0
	Ozokerite	2.0
	Carnauba wax	4.0
	Spermaceti	2.0
	Cocoa butter	1.5
	Lanolin	2.5
	Colors	23.0
(V)	Dextran palmitate as in Formula I	60.0
	Bentonite	20.0
	Colors	20.0
(VI)	Dextran palmitate as in Formula I	40.0
	Bentonite	27.5
	Poinceau 3 R	9.5
	Certified amaranth	5.5
	Yellow ochre	10.5
	Petrolatum	7.0

The ingredients of these respective formulae are compounded by heating the dextran ester to convert it to a fluid or plastic state, and then distributing the coloring matter or dye through the fluid or plastic mass. If inerts such as talc, bentonite, etc. are to be included these may be ball milled with the coloring matter or dye before being mixed with the fluid dextran ester, at a temperature at which the ester remains readily workable. A heated, water-jacketed mixer or a heat-jacketed paint mill can be used to insure intimate commingling of the ingredients. The mass, while plastic, is given the desired shape. These compositions may take the form of cakes, blocks, balls, pencils, sticks, creams or liquids of emulsion or suspension type. The plastic moldable compositions may be compressed or extruded through dies of appropriate shape to obtain continuous rods of corresponding cross-section and the rods may be cut into lengths to obtain discs or "cakes," or the lengths may be beveled and mounted in lipstick holders.

The final product may have a consistency such that it can be taken up by the fingers or a cosmetician's brush and spread on the skin or lips, or sticks may be applied directly to the skin. In the use of a lipstick in accordance with the invention, the stick is manipulated to apply a color coating to the lips. Since the dextran fatty acid esters employed as base or binder for the color and inerts, if the latter are present, are water-repellent, the ester is not readily smeared or dissolved by liquids, hot or cold, and thus the coloring matter intimately associated with the dextran ester film, tends to remain on the lips

for a long time, even when the coloring matter is not a stain.

The proportion of dextran higher fatty acid ester in the preparation may vary. It will usually comprise at least 50% by weight of the total composition, but this is not essential and lesser amounts of the ester may be used, especially when the product is a cream containing a high percentage of oils and intended for use as a skin lubricant.

Instead of esters of the higher fatty acids with dextrans, we may use those esters of dextran conversion products which are physiologically harmless such as lower acyl esters of dextran having from 1 to 5 carbon atoms in the acyl groups, alkyl dextrans such as those containing 1–5 carbon atoms in the alkyl radical, carboxyalkyl and hydroxyalkyl dextrans in which the alkyl portion of the carboxyalkyl or hydroxyalkyl group has from 1 to 5 carbons and particularly carboxymethyl dextrans and hydroxyethyl dextrans. The esters of the conversion products may contain an average of from less than 1.0 to 2.9, preferably to 2.5 of the higher fatty acid radicals and from less than 1.0 to 2.9, preferably to 2.5 of the lower acyl, alkyl, carboxyalkyl, hydroxyalkyl or other groups, per anhydroglucopyranosidic unit. Preferably, the esterified conversion products contain from less than 1.0 to 1.5 of the radicals other than the higher fatty acid radicals and from about 1.5 to 2.5 of the higher fatty acid radicals, the total number of substituent groups per anhydroglucopyranosidic unit of the dextran being not greater than 3.0. The esters of the conversion products may have a controlled moisture pick-up and retention capacity rendering them suitable for combination with agents to be released gradually when the composition is contacted by moisture. Esters of carboxymethyl and hydroxyethyl dextrans are typical esters of that type.

It will be apparent that by selection of the dextran ester (both the dextran and the esterifying acid or chloride, as well as the D. S. being involved and variable), used in the cosmetic preparations, and by incorporating therein other agents including natural waxes and oils, fats, etc., it is possible to vary the hardness of the preparation, its sensitivity to moisture and other physical properties, so that a wide range of cosmetic products are possible.

These selections, variations and modifications may be made without departing from the spirit and scope of the invention and therefore it is to be understood that the invention is not to be limited except as defined by the appended claims.

We claim:

1. A lipstick comprising coloring matter and a base comprising an ester of a dextran with a saturated fatty acid of from 14 to 18 carbon atoms, said ester containing an average of from 2.5 to 3.0 of the fatty acid radicals per anhydroglucopyranosidic unit.

2. A lipstick comprising coloring matter and a base comprising dextran palmitate containing an average of 2.5 to about 3.0 palmitoyl groups per anhydroglucopyranosidic unit.

3. A lipstick comprising coloring matter and a base comprising a palmitate of carboxymethyl dextran containing an average of 2.5 to about 3.0 palmitoyl radicals per anhydroglucopyranosidic unit.

4. A lipstick comprising coloring matter and a base comprising an ester of a dextran with a saturated fatty acid of from 8 to 18 carbon atoms, said ester containing an average of less than 1.0 up to 3.0 of the fatty acid radicals per anhydroglucopyranosidic unit.

5. A lipstick comprising coloring matter and a base comprising an ester of a dextran with a saturated fatty acid of from 14 to 18 carbon atoms, said ester containing an average of less than 1.0 up to 3.0 of the fatty acid radicals per anhydroglucopyranosidic unit.

6. A lipstick comprising coloring matter and a base comprising a dextran palmitate containing an average of less than 1.0 up to 3.0 palmitoyl radicals per anhydroglucopyranosidic unit.

7. A lipstick comprising coloring matter and a base comprising a dextran stearate containing an average of less than 1.0 up to 3.0 stearoyl radicals per anhydroglucopyranosidic unit.

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