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COSMETIC PREPARATION AND PROCESS FOR MANUFACTURE THEREOF

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7 Claims. (Cl. 167—90)

This invention relates to a cosmetic for application to the human skin. More particularly the invention is a stable cosmetic emulsion of a degree of controlled acidity approximating that of normal human skin and possessed of substantial neutralizing power sufficient to return to its normal, acid condition skin that has become abnormally alkaline or acidic. The controlled acidity of the emulsion and its desirable neutralizing power are attributable to a special buffering system comprising a water soluble ionizable inorganic gluconate salt and gluconic acid. Also included within the invention is a process of making such a stable cosmetic emulsion.

The literature and the patents on cosmetics contain disclosures of the results of research on the effects of pH changes on human skin. It has been conclusively established that the average person has a normal pH on the acid side, almost always between 3.2 and 7 and usually between 4 and 6. Most researchers and practicing physicians are agreed that the acidic pH or "acid mantle" of the dermal surfaces tends to inhibit bacterial growth. Some have shown that alkaline pH's are destructive of epidermal cells, cause erythema and tend to be irritating to the derma, the effects of these actions being especially pronounced on sensitive skins. For these reasons there has come into use a number of acidic cosmetic products intended to help maintain the skin at an acidic pH, while still effecting their cosmetic function.

Because the hands are the parts of the body that most frequently come in contact with external surfaces and media which are of alkaline pH's and because they are often immersed in alkaline solutions that tend to remove natural oils and emollients from the skin, hand lotions are cosmetic products in which it is especially desirable to maintain an acidic pH. Acidic hand lotions containing organic acids, in which group gluconic acid is included, have been prepared for this purpose.

In the manufacture of acid hand lotions and other acidic emulsions there are frequently encountered serious problems in obtaining a sufficiently stable emulsion so that the product will remain attractive in appearance over long periods of storage and will not separate or otherwise give evidence of instability. The combination of acidic ingredients and the amounts thereof used to acidify the lotion or, more accurately, acidify the hydrophilic phase, must be one which is of acceptable compatibility. Similarly, emulsifiers to be employed are chosen for their compatibility with oil and water under acidic conditions. The ordinary fatty acid soaps, which are among the most frequently employed emulsifiers in the cosmetic art, are alkaline in solution and are considered unsuitable for use in acidic emulsions because they lose emulsifying power and break down to form water-insoluble fatty acids or acid soaps.

Now, in accordance with the present invention, there is provided a stable acidic cosmetic emulsion preparation for the skin comprising an aqueous hydrophilic phase, with a lipophilic phase and an emulsifier to maintain said phases in stable emulsion form, the hydrophilic phase being at a pH above 3 and containing a minor proportion, in combination less than about 10% of the lotion, of gluconic acid and soluble metallic gluconate salt. It has been found that gluconic acid combined with such gluconate has greater neutralizing effect in such lotions

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that many other organic acids and buffer systems which have been included in emulsion cosmetics, while still being of acceptable initial acidity. Thus, where other skin lotions fail to lower abnormal skin pH to the desired acidity a comparable composition, but containing gluconic acid and metallic gluconate, does return the skin to the desired pH. In addition, the gluconic acid is readily soluble in the aqueous phase of aqueous emulsions, is odorless and practicallly tasteless, is compatible with perfumes for cosmetics, its sequestration of traces of heavy metals also aiding in stabilizing the perfumes and cosmetic ingredients, and perhaps most important, it is stable in a wide variety of cosmetic emulsions.

The presence of gluconic acid in the present hand lotion enables that lotion to exert a considerable neutralizing effect on skin that has become basic due to contact with soaps, detergents, and other alkaline materials. A major function of these hand lotions is to counteract alkalinity, but the cosmetic preparation should also be of effect against excess acidity. To obtain a lotion which resists pH change in either direction there is present in the invented compositions a combination of gluconic acid and water-soluble metallic gluconic acid salt. The latter term describes a metal salt of gluconic acid, usually alkali metal, preferably sodium or potassium. The salt may be added directly or may be made by neutralization of gluconic acid with an alkaline agent, such as a strong base. The neutralizing material is preferably a metallic alkaline compound, most preferably of an alkali metal, such as sodium or potassium, usually added as the hydroxide, carbonate or bicarbonate. The gluconic acid may be added as its lactone, preferably glucono-delta-lactone, which hydrolyzes in aqueous media to produce an equilibrium mixture of gluconic acid and lactone. A mixture of lactone, gluconic acid and metallic gluconate can also be made by admixing the lactone and a salt-forming base with the other hand lotion ingredients.

Cosmetic emulsions are generally aqueous emulsions of either the oil-in-water or water-in-oil types, the former usually being the relatively thin lotions and the latter classification usually describing the physical nature of cosmetic creams. In both types of emulsions there is found a hydrophilic phase mixed with a lipophilic phase. In the oil-in-water emulsions, as indicated by the name, the lipophilic material is in the dispersed phase while the hydrophilic or aqueous substances comprise the continuous phase. The converse is true for water-in-oil preparations. Although the presently disclosed gluconic acid constituent is useful in both creams and lotions, its stability is most valuable in the lotion compositions because, being relatively fluid, these products are most susceptible to separation and reactions of ingredients which might promote separation. Although acid creams other than those acidified with the compounds employed in this invention also can deteriorate or otherwise become unattractive on storage, their lack of mobility often hinders separation.

The lipophilic phase of cosmetic hand lotions usually constitutes a minor proportion of the lotion, generally from 1 to 10% by weight thereof. In this phase there are included the conventional oleaginous base materials such as mineral oil, higher fatty alcohol, partial esters of polyhydric alcohol, e.g., glyceryl monostearate, propylene glycol monolaurate, diglycerides, to name only a few, triglycerides, higher fatty acid esters or waxes, and other lipophiles. Some of these so-called lipophilic materials possess hydrophilic functional groups which make them compatible with the continuous aqueous medium. Thus, the partial esters are also used as emulsifiers for oleaginous ingredients. Perfumes, emollients, such as lanolin, and antioxidants, such as lecithin, are also found in the oily phase.

The continuous aqueous phase is composed substantially of water although it will also contain those ingredients of the lotion which are preferentially soluble in water. Among these may be mentioned the common solvents, such as the lower alcohols, including ethanol, lower polyhydric alcohols, propylene glycol, water soluble salts, both inorganic and organic water soluble acids, dyes, germicides, surface active agents and emulsifiers. Of course, although many compounds are either strictly hydrophobic or lipophilic, others possess dual characteristics and, in equilibrium dispersion or emulsion, will be found distributed between the two phases. However, in this specification, for the sake of clarity of presentation, those materials which are predominately of one of these characteristics are so classified. Thus, although some lower alcohol may be found in the aqueous medium, such diverse solubility and action will be ignored.

To promote the dispersion of one phase in the other, it is generally desirable to employ an emulsifying agent. Such compounds have both hydrophilic and hydrophobic elements and act as links between the oily and aqueous constituents of the emulsion. In the present compositions it is highly preferable to use nonionic emulsifiers, such as the partial esters of higher fatty acids with polyhydric alcohols, previously mentioned, long chain polyoxyalkylene polymers containing hydrophobic and hydrophilic groups in balance, the so-called self-emulsifying waxes and other suitable surface active agents, such as the polyoxyethylene esters and ethers of higher fatty alcohols or alkyl phenols, the block copolymers of different lower alkylene oxides (the Pluronics), sugar esters and ethers and so forth.

Although the non-ionic emulsifiers and so-called self-emulsifying waxes are highly preferred emulsifying agents for the present cosmetic lotions, anionic or cationic surface active compounds may also be usefully employed if they are chosen with care for resistance to decomposition in acidic media. Thus, in hand lotions that are of only relatively slight acidity there may be employed, as emulsifiers, monoglyceride sulfates and sulfonates, the alkyl ether sulfates and sulfonates, the di-alkyl sulfosuccinates, higher fatty alcohol sulfates and other well known acid-resistant surfactants. Cationic agents having surface activity are also effective emulsifiers in hand lotions. The cationic compounds are usually employed in conjunction with non-ionics and the presence of anionic materials is generally avoided when cationic materials are used because of the interaction of these two types of emulsifiers, usually accompanied by the production of an insoluble precipitate of low or negligible dispersing power. The cationic emulsifiers of the quaternary ammonium type possess strong anti-bacterial power and therefore are of additional desirable utility in hand lotions. Among the cationics that may be used there may be listed, as examples, N-lauroyl colamino formylmethyl pyridinium chloride, cetyl trimethyl ammonium bromide and diisobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride. These compounds are of a high degree of stability in the presence of gluconic acid and water soluble inorganic gluconate salt.

Gluconic acid, which is the major acidifying agent of these hand lotions, is soluble in water but not in alcohol, ether or most other organic solvents. Gluconic acid may be added directly to the aqueous phase of the hand lotions or to the emulsion after it is formed, although the latter course is generally considered to be preferable. Instead of using the gluconic acid syrup, the easily handled crystalline lactone of gluconic acid, glucono-delta-lactone, may be employed. The lactone hydrolyzes in aqueous solution with formation of the acid and establishment of an equilibrium between the acid and the delta- and gamma-lactones. Hand lotions containing either the gluconic acid ingredient or the equilibrium mixture referred to are resistant to an increase in pH and even when subjected to alkaline agents tend to maintain their original pH or else to allow it to be increased only slightly. When such lotions are applied to skin that has been subjected to alkaline solutions a small quantity of lotion lowers the skin pH to a point near the pH of the lotion itself, restoring the protective acid condition of the skin. The presence of the gluconic acid also tends to stabilize the acid pH of the lotion by minimizing the effect of alkaline materials, whether they are in the lotion formula or contact the lotion or develop within it during manufacture or storage. These compounds also sequester metal ions which otherwise might tend to react to form unwanted colored compounds or which might catalyze decomposition of lotion components and breaking of the emulsion.

The pH at which it is desired to maintain the hand lotion and the buffering activity of the lotion can be adjusted by varying the quantities and proportions of gluconic acid and water-soluble metallic gluconate salt in the formula. The addition of gluconate such as the sodium or potassium compound tends to establish a new equilibrium pH, higher than that of the gluconic acid alone. It also gives the lotion increased resistance to alteration of pH by acid. Instead of adding the gluconate as its salt it can be made by neutralization of gluconic acid or the lactone by any suitable alkaline salt-forming material such as sodium hydroxide, sodium carbonate, alkali metal bicarbonate and so forth.

In cosmetic lotions it is preferred to keep the amounts of emulsifiers and other adjuvant materials to the necessary minimum so as to limit their effects on the skin and prevent deposition of relatively large amounts of insoluble substances on the epidermis. Such limitation also allows the oil, emollient and aqueous ingredients to better perform their own designed functions on the skin. Gluconic acid and its salts may be used in cosmetic emulsions up to a limit of about 10% of the said compositions. Above that concentration the salt and acid content tends to be too great to be compatible with many cosmetic lotions and interferes with the desired properties of the lotion. The lower limit of gluconic acid and gluconate content may be as little as 1/10 of 1%, so long as that proportion has an acidifying effect on the lotion. On a hand lotion basis it is preferred to employ from 1 to 7% of a combination of gluconic acid and soluble inorganic gluconate and/or glucono-lactone. The amount of gluconic acid, salt, and/or lactone should be such as to result in a lotion pH above 3. Below that pH the acid lotion tends to irritate rather than soothe the skin. Although the skin itself contains buffering agents and the normal, small amounts of lotion employed usually will not lower the pH all the way to that of the lotion itself, it is considered that as a protection against application of excessive amounts of lotion the pH thereof must be kept above 3. Most formulations for general cosmetic use will have a pH above about 3.5 and one of the pH 4 to 6 will closely match that of the average human skin. A lotion of pH 4 will conform to skin pH and will also be of considerable effectiveness against alkaline skin conditions.

A lotion of a pH below 4, even below 3.5 may be useful for application to the hands after subjecting them to highly alkaline solutions, such as solutions of some harsh detergent compositions. The lotion will acidify the skin but the final skin pH will be higher than that of the cosmetic, and nearer to that of normal skin. Such lotions are also suitable for ordinary cosmetic use on the hands in many instances because the natural buffering agents deposited by perspiration on the skin, will tend to limit the extent to which the lotion can lower the skin acidity. To keep the lotion at a suitable pH and maximize its effectiveness against alkalinity it has been found that the amount of metallic gluconate should be less than that of the gluconic acid or sum of gluconic acid and lactone.

The preferred oil-in-water skin lotions should comprise a major proportion of continuous aqueous hydrophilic

phase and a minor proportion of lipophilic phase. Usually the aqueous phase is almost entirely water and constitutes over 75%, most often 75 to 95% of the lotion. The lipophilic part of these emulsions, which is the minor phase, usually constitutes less than 25% of the composition, most often 1 to 10% and sometimes as little as 2 to 5%. The gluconic acid, inorganic gluconate and lactone, if present, are in the aqueous phase and preferably are less than 10% of that phase of the hand lotion. They are present in sufficient quantity to desirably adjust the acidity of the aqueous phase although they have limited effect on the pH of the dispersed phase. This difference in acidification allows the use of some fatty lipophilic materials in the less acidic oil phase, even though they would tend to decompose at the lower pH's of the aqueous phase. The alkaline materials deposited on the skin after immersion in strong washing solution and the acids to which the hands might become exposed are generally water soluble and therefore are rapidly neutralizable by the gluconic compounds.

When making the present skin lotions it is preferred to heat the components of the aqueous and lipophilic phases separately to an elevated temperature, usually above 150° F., at which the phases are homogeneous. At such a temperature, e.g., 180° F., the phases are admixed with good agitation to form the emulsion. This emulsion is cooled somewhat, usually to a temperature below 150° F., and an aqueous solution of gluconic acid and inorganic gluconate, omitted from the aqueous phase, are added to it. With lotions that are inherently less stable and more difficult to form or more likely to break when subjected to acidity it may be preferable to add the gluconic compound as the lactone, with soluble neutralizing agent or inorganic gluconate salt, to avoid a quick change in pH of the aqueous phase. Gradual in situ acidification of the lotion during cooling might very well maintain emulsion stability when quick acid addition could tend to break the emulsion. To insure that the lactone has not been substantially hydrolyzed to the acid, which might possibly break the emulsion, it should be added to the emulsion or aqueous phase in an aqueous solution as soon as possible after having been dissolved, usually within about 2 to 10 minutes. Alternatively, it can be added as a solid to the aqueous phase before emulsification. In either case the object is to have the glucono-delta-lactone in the emulsion as quickly as possible before it starts to hydrolyze to the acid. Other ingredients may be added as soon as the gluconic compound has been incorporated in the emulsion or after additional cooling. Minor amounts of heat-sensitive adjuvants such as perfumes, antibiotics, germicides and colorants may be added at lower temperatures, e.g., room temperature.

The following examples are given to illustrate the invention. In the examples, specification and claims all parts are by weight unless otherwise specifically indicated.

EXAMPLE I

An acid hand lotion was made according to the following formula:

	Percent
Part A:	
Water	80.0
Quaternary ammonium salt	1.5
Polyethylene glycol of molecular weight 1500	0.5

Propylene glycol (humectant, solvent)	5.0
Polyoxyalkylene ester	0.03
Part B:	
Mineral oil	1.0
Lanolin	0.5
Higher fatty alcohol (cetyl alcohol)	0.5
Polymethyl siloxane	1.0
Self-emulsifying waxy condensation product of higher fatty alcohol and ethylene oxide	1.0
Part C:	
Water	5.0
Glucono-delta-lactone	3.0
Sodium hydroxide	0.25
Part D:	
Perfume	q. s.
Dye	q. s.

Parts A and B were each heated to 180° F. at which temperature B was added to A and stirred for about 5 minutes. The emulsion formed and was cooled to 140° F. and then part C, at room temperature, was admixed with A+B, only about 5 minutes after the making of C. After cooling to 95° F. the emulsion was perfumed and colored by addition of part D. The complete lotion was then cooled to 80° F. and stirring was continued for an additional ½ hour, after which it was ready for packaging in either conventional glass bottles, resilient plastic squeeze containers or pressurized "aerosol" containers, as desired.

The finished hand lotion was tested for its pH stability to alkalinity. In this test 10 grams of lotion were diluted with 50 ml. of water and the diluted emulsion was titrated with 0.01 N NaOH. Even after the addition of 150 ml. of this caustic solution (pH 12.0) the pH of the diluted emulsion was only 5.4. A similar experiment, in which there was employed a much greater molar concentration of another organic acid, well known for acidifying cosmetics, resulted in a pH of 10.2. Both lotions had approximately the same initial pH's, that of the invented composition being slightly higher, at 3.6.

In a series of in vivo tests the ability of the lotion to rectify abnormal alkalinity of the skin was recorded. In these tests the normal pH of the skin on the back of the subject's hand was measured with a pH meter (Industrial Model M, Beckman Instrument Co.). The hands were then soaked for 5 minutes at 105–115° F. in a 0.5% solution of bland soap, following which they were rinsed in running tap water and towel dried. The skin pH was determined immediately after drying and 5, 15, 30 and 60 minutes later after subsequent application of lotion. The following table summarizes results of these tests:

Table 1

Total subjects	Total hands tested	Initial pH, before soaking (avg.)	Abnormal pH, after soaking (avg.)	Lotion applied (drops/hand)	Skin pH (avg.) at time (min.) after application of lotion				
					0	5	15	30	60
6	12	4.8	7.5	2	4.2	4.4	4.5	4.7	4.8
2	4	4.9	7.3	4	3.8	4.1	4.1	4.2	4.3

In control experiments in which the same procedure was carried out except for application of the lotion it took over an hour for the skin pH to decrease to approximately its initial level.

Although the above lotion was formulated primarily to be effective against alkali on the skin, it also had an appreciable action against excess acidity, which action could be increased by raising the amount of sodium gluconate in the formula and increasing the ratio of gluconate to gluconic acid present.

EXAMPLE II

A cosmetic lotion for counteracting alkalinity of skin

surfaces to which it is applied was made of essentially the same formula as that of Example I except that 6% glucono-delta-lactone and 0.5% sodium hydroxide were included, the water content of the lotion being decreased to compensate for the additional amounts of lactone and hydroxide. No perfume or colorant was added. The lotion was manufactured according to the process of Example I with the omission of the addition of the part D ingredients at 95° F.

The product was a stable acidic lotion of high alkali neutralizing activity. When tested by alkali addition, according to the method of Example I, 10 ml. of lotion, initially at pH 3.7 was increased to a pH of only 4.7 after treatment with 150 ml. of 0.01 N NaOH.

EXAMPLE III

A hand lotion was made according to a formula essentially the same as that of Example II except that 6.5% of gluconic acid was employed instead of the 6.0% of glucono-delta-lactone. The manufacturing process was the same. The product made was a lotion of acceptable stability and excellent neutralizing effect against alkali.

Various compatible adjuvants may be added to the invented lotions for their special effects or properties. Their addition may be made at any suitable stage of the processing and the manufacturing procedure may be adjusted, if desirable, to better effect admixing of adjuvant and to maintain stability of the lotion. As illustrative of such additives may be mentioned bactericides, e.g., hexachlorophene; preservatives, to combat mold and bacterial growth, e.g., methyl and propyl para-hydroxybenzoate, skin restoratives; e.g., allantoin; skin rejuvenators, e.g., steroids; deodorants; thickening agents, e.g., hydroxy alkyl celluloses; humectants, e.g., sorbitol; and opacifiers, e.g., behenic acid.

The above invention has been described in conjunction with illustrative examples thereof. It will be obvious to those skilled in the art who read this specification that other variations and modifications of the invention can be made and various equivalents substituted therein without departing from the principles disclosed or going outside the scope of the invention or purview of the claims.

What is claimed is:

1. A stable acidic cosmetic emulsion lotion for the skin comprising an aqueous hydrophilic phase, a lipophilic phase and an emulsifier to maintain said phases in stable emulsion form, the hydrophilic phase being at a pH above 3 and containing a minor proportion, in combination less than about 10% of the lotion, of gluconic acid and soluble metallic gluconate salt.

2. A stable acidic hand lotion comprising an oil-in-water emulsion having a major proportion of a continuous aqueous hydrophilic phase, a minor proportion of dispersed lipophilic phase and a nonionic emulsifier distributed between the phases and maintaining them in stable emulsion form, the hydrophilic phase being at a pH above 3 and containing a minor proportion, less than 10% of the lotion, of a mixture of gluconic acid, soluble alkali metal gluconate and lactone of gluconic acid.

3. A stable acidic hand lotion comprising an oil-in-water emulsion having a major proportion, over 75%, of a continuous aqueous hydrophilic phase, a minor proportion, less than 25%, of a lipophilic phase and a non-

ionic emulsifier distributed between the phases and maintaining them in stable emulsion form, the hydrophilic phase being at a pH of about 4 to 6 and containing a minor proportion, less than 10% of the hand lotion, of an equilibrium mixture of gluconic acid, soluble alkali metal gluconate salt and lactone of gluconic acid, in which mixture the alkali metal gluconate salt is a minor constituent.

4. A stable acidic hand lotion comprising an oil-in-water emulsion containing 75 to 95% water and minor proportions of oleaginous base, lanolin, and non-ionic emulsifier distributed between the phases and maintaining them in stable emulsion form, the continuous aqueous hydrophilic phase of the emulsion being at a pH of about 4 to 6 and containing a minor proportion, less than 10% of the hand lotion, of an equilibrium mixture of gluconic acid, soluble alkali metal gluconate salt and lactone of gluconic acid, the amount of gluconate being less than the sum of gluconic acid and lactone of gluconic acid.

5. A process for manufacturing a stable acidic cosmetic emulsion which comprises admixing and emulsifying water, oleaginous base and nonionic emulsifier, adding substantially unhydrolyzed glucono-delta-lactone as a source of hydrogen ions, the lactone hydrolyzing to form gluconic acid in situ, after formation of the emulsion, in sufficient amount to produce a stable acidic product.

6. A process for manufacturing a stable acidic cosmetic emulsion of aqueous hydrophilic phase and lipophilic phase which comprises mixing and emulsifying aqueous hydrophilic and lipophilic phases with nonionic emulsifier at a temperature at which the lipophilic phase is liquid and is emulsifiable with the aqueous phase, making an aqueous solution of glucono-delta-lactone and admixing lactone solution and emulsion at a temperature at which the solution is emulsified, before the lactone has hydrolyzed sufficiently to gluconic acid to decrease stability of the emulsion.

7. A process for manufacturing a stable acidic cosmetic oil-in-water emulsion hand lotion which comprises mixing substantially all the lipophilic and hydrophilic constituents of such a lotion in separate lipophilic and hydrophilic phases, mixing and emulsifying these phases with nonionic emulsifier at a temperature above 150° F., making an aqueous solution of glucono-delta-lactone and soluble salt forming metallic neutralizing agent for gluconic acid, cooling the emulsion below 150° F. and adding the solution thereto before the lactone has been substantially hydrolyzed to gluconic acid.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,060,096

October 23, 1962

Ling Wei

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 1, line 66, strike out "with"; column 5, line 70, for "acid" read -- acidic --; column 6, line 19, strike out "and".

Signed and sealed this 7th day of April 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents