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2,487,558

CREAM DEPILETORY AND PROCESS FOR PREPARING SAME

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2 Claims. (Cl. 167-89)

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The present invention relates to a cream depilatory and to the process for preparing same. More particularly, it relates to a depilatory preparation in cream or paste form suitable for use on the human skin (as, for instance, in the removal of hair from the forearms, legs, armpits, etc.) and to a simple and efficient process for preparing same. It has for its purpose the provision of a cream depilatory of good stability, high cosmetic acceptability, low cost and rapid effectiveness which is devoid of many of the disadvantages of previous preparations of this nature and which will remove hair from the human skin with safety, speed and facility.

While mechanical depilatories (such as waxes and resins applied while warm and then removed upon cooling) are known and used to some extent, most of the depilatories in common use at the present time are chemical in nature.

The reaction mechanism of these chemical depilatories is fairly well known. Marriott (Journ. Intern. Soc. Leather Trades Chem. 17, 178-193 (1933)) and others have pointed out that the beginning of effective depilation occurs when the disulfide linkages in the cystine component of the keratin molecule in hair are reduced. When these disulfide linkages of the cystine are broken, the combination of the free sulfhydryl degradation products with the alkali present in the depilatory causes swelling of the hair and ultimate disintegration.

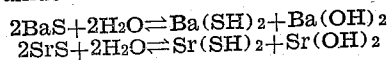
Thus, an effective depilatory must contain (a) a reducing agent sufficiently potent to reduce the disulfide linkages of cystine in the hair to cysteine, and (b) an agent of sufficient alkalinity to cause the swelling of a reduced keratinous protein.

The most commonly used reducing agents in cosmetic depilatories have heretofore been the sulfides and the hydrosulfides of the alkaline earths. The alkali metal sulfides hydrolyze quite readily to give equilibrium mixtures containing alkali metal hydrosulfides, which are good reducing agents and excellent depilatories, but the alkali metal hydroxides formed as concomitants are excessively caustic and irritating to the human skin. The alkali metal hydrosulfides per se are used to some extent in conjunction with alkali earth metal hydroxides, but their use in cosmetic depilatories is limited by their poor stability and their excessive hydrogen sulfide odor.

The alkali earth metal sulfides, however, do not possess these disadvantages to the same marked degree. Thus, barium sulfide and strontium sulfide are relatively stable and not excessively malodorous. When suspended in

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water, these alkali earth sulfides hydrolyze to form equilibrium mixtures of alkali earth metal hydrosulfide and alkali earth metal hydroxide:



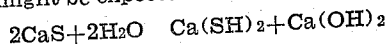
The alkali earth metal hydrosulfides thus formed serve as potent reducing agents, while the alkali earth metal hydroxides provide the alkalinity required for effective depilation.

In terms of hydrogen ion concentration, no depilation will occur at a pH below 11. For rapid and effective epilation, a pH of 12 to 13 is required (De Navarre, The Chemistry and Manufacture of Cosmetics, D. Van Nostrand Co. 1941) page 535. A saturated aqueous solution of $\text{Ca}(\text{OH})_2$ has a pH of 12.4; a saturated aqueous solution of $\text{Sr}(\text{OH})_2$ has a pH of 12.9; a 0.1 N (1.58%) aqueous solution of $\text{Ba}(\text{OH})_2$ has a pH of 13.1.

While used to some extent in cosmetic depilatories, barium sulfide has the disadvantage of being poisonous, whereas strontium sulfide is excessively expensive and often difficultly available. Both of these compounds have rather high molecular weights so that comparatively large quantities of either must be employed to obtain an effective concentration of active sulfhydryl group. Thus, pure barium sulfide contains only 18.9% of sulfur and pure strontium sulfide contains only 26.8% of sulfur. These compounds are furthermore rarely available in the pure form; products of commerce often contain as little as 65% of the pure sulfide, the remainder being inert ingredients.

Calcium sulfide would indeed be the ideal depilating agent. The compound is cheap and readily available in large amounts. When pure, calcium sulfide contains 44.5% of sulfur. However, when technical calcium sulfide is used in a depilatory preparation, it is most surprisingly and completely ineffective.

Calcium sulfide is made industrially by reducing calcium sulfate with carbonaceous material or by the fusion of lime and sulfur, both at advanced temperatures (Ullmann's Enzyklopaedie der Technischen Chemie, volume 3, page 58, 1929). When prepared in this manner, calcium sulfide forms a yellowish to light-gray powder. Upon suspension in water, it fails to hydrolyze to calcium hydrosulfide and calcium hydroxide as might be expected:



This unforeseen behavior may be attributed to the deposition of a surface layer of poorly soluble

calcium hydroxide on each discrete particle of calcium sulfide. In other words, the hydrolysis does commence when the calcium sulfide is suspended in water, but is prevented from proceeding to the building up of an effective concentration of calcium hydrosulfide by the accumulation of an insoluble or poorly soluble film of calcium hydroxide at the water-solid interface, which film prevents further solution and hydrolysis.

To overcome this difficulty, it becomes necessary to prepare the calcium hydrosulfide-calcium hydroxide couple in aqueous solution-suspension, rather than by hydrolysis of preformed calcium sulfide. Thus, Donner (U. S. Patent 1,379,855, 1921) passes hydrogen sulfide gas into an aqueous suspension of milk of lime to obtain the desired equilibrium mixture of calcium hydrosulfide and calcium hydroxide. Related preparative procedures are described by Divers and Shimidzu (Journ. Chem. Soc. (London) 45, 270 (1884)) and by Hartman (Canadian Patent 438,318 (1946)). From a practical point of view, this procedure has many disadvantages:

(a) Hydrogen sulfide is noisome and a noxious gas and its use in a cosmetic manufacturing plant is highly undesirable;

(b) Because of the insolubility of the calcium hydroxide, the uniform "gassing" of a slaked lime suspension is not usually feasible, so that duplicate batches of $\text{Ca}(\text{SH})_2$ - $\text{Ca}(\text{OH})_2$ are rarely of identical composition;

(c) Unless accurate control of the "gassing" is feasible, there is often the danger of carrying the process too far and thus imparting a most undesirable hydrogen sulfide odor to the finished product;

(d) Chemical lime usually contains traces of heavy metal compounds such as iron oxides, etc., which impart to the finished depilatory product most undesirable gray, green or blue off-colorations due to the highly-colored heavy metal sulfides formed by interaction with the hydrogen sulfide.

It is a purpose of the present invention to provide a cream depilatory based on a manufacturing procedure which takes advantage of the high effectiveness of depilatories based on calcium hydrosulfide-calcium hydroxide, their low cost, their lack of excessive causticity and irritating effects on the human skin and their high effective sulphydryl concentrations but which obviates completely (a) the necessity of "gassing" a lime suspension with hydrogen sulfide, (b) the lack of uniformity in previous products of this nature, (c) the marked hydrogen sulfide odor of improperly "gassed" batches, (d) as much as possible, the off-colored heavy metal sulfide impurities, (e) the noisome and noxious features of the previous manufacturing procedures, and such other objections which have previously been attributable to the group of depilatories based on calcium hydrosulfide-calcium hydroxide.

Other reducing agents have also been used in cosmetic depilatories in place of the alkali earth metal sulfides and hydrosulfides. Among these may be mentioned:

(a) The alkaline stannites (Stoddard and Berlin, U. S. Patents 2,123,214 (1938); 2,199,249 (1940); McKee and Morse, U. S. Patent 1,899,707 (1933)). These are excessively unstable and require too high alkalinity and too long a contact period on the skin for effective cosmetic use;

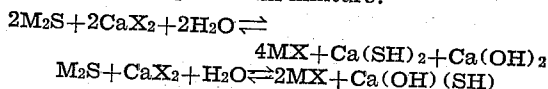
(b) Alkyl and aryl mercaptans in alkaline media (Jaeger and Herrlinger, U. S. Patents 2,169,147-8 (1939); Turley and Windus, U. S. 75

Patent 1,973,130 (1934)). These are usually excessively malodorous and therefore unsuited for cosmetic purposes;

(c) The alkaline salts of thioglycollic acid (Fletcher, French Patent 824,804 (1938); Boheman, British Patent 484,467 (1938); Evans and McDonough, French Patent 844,629 (1939); U. S. Patent 2,352,524 (1944)). While these depilatories represent a considerable advance in the cosmetic art, they are still considerably more expensive than those based on calcium hydrosulfide-calcium hydroxide, and are excessively subject to inactivation by the oxygen of the air, which converts the thioglycollic acid derivative to inactive thio-diglycollic acid and dithio-diglycollic acid derivatives;

(d) Sodium selenide (Na_2Se), (Silman, Deutsche Parfumerie, 17,316 (1931) which is an effective depilatory, but quite unstable and excessively toxic.

The basis of the present invention is my finding that an excellent depilatory preparation can be based on the products obtained by the reaction of a solution of a water-soluble sulfide and a solution of at least an equimolecular quantity of a water-soluble calcium salt. Thus, when an aqueous solution of a water-soluble sulfide is mixed with a solution of at least an equimolecular quantity of a water-soluble calcium salt, there is no precipitation of calcium sulfide as might be expected. Instead, there is formed the following equilibrium mixture:



where M is an equivalent of the cation of the water-soluble sulfide and X is an equivalent of the anion of the water-soluble calcium salt. This equilibrium mixture contains both of the components necessary for effective depilation, i. e. the reducing agent—calcium hydrosulfide, and the alkaline agent—calcium hydroxide, which gives the medium the necessary pH between 12 and 13 without being excessively caustic and irritating to the human skin.

Typical examples of water-soluble sulfides effective in the process of the present invention are sodium sulfide, ammonium sulfide, potassium sulfide, lithium sulfide, and organic sulfides such as ethanolanmonium sulfide, diethanolanmonium sulfide, triethanolanmonium sulfide, ethylene diammonium disulfide, morpholinium sulfide, methylammonium sulfide, etc., etc. The preferred product for the present invention is a flaked sodium sulfide, substantially free of iron and other heavy metal impurities, assaying 60%-61% Na_2S , such as is marketed by the Barium Reduction Company, South Charleston, West Virginia.

Typical examples of water-soluble calcium salts effective in the process of the present invention are calcium chloride, calcium bromide, calcium iodine, calcium nitrate, calcium nitrite, calcium acetate, calcium gluconate, calcium levulinate, etc., etc. The preferred product for the present invention is the technical, flaked calcium chloride obtained as a uniform, low-priced by-product from the Solvay soda ash process and assaying 75%-77% of calcium chloride, corresponding to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

The concentrations of water-soluble sulfide in the finished cream depilatory may vary from 0.08 gram-mole to 1.50 gram-moles per kilogram of product, but the preferred concentration for

a speedy, effective and safe depilation is from 0.30 to 0.50 gram-mole per kilogram of finished product. In every case, at least an equimolar concentration of water-soluble calcium salt is employed. A slight molar excess of calcium salt is permissible, but it is undesirable to have an excess of water-soluble sulfide. If the sulfide is an alkali metal sulfide, the excess will render the product more caustic and more irritating to the human skin. If the sulfide is an ammonium or an organic sulfide, its tendency to decompose upon standing will impart an undesirable odor to the finished depilatory product.

It will thus be recognized that by the simple expedient of mixing two easily prepared solutions of readily available and inexpensive chemicals:

(a) An equilibrium mixture containing calcium hydrosulfide, calcium hydroxide and basic calcium hydrosulfide $[Ca(SH)(OH)]$ is prepared without the necessity of "gassing" a suspension of lime with hydrogen sulfide;

(b) A product of invariable uniformity can be obtained;

(c) An excess of malodorous hydrogen sulfide in the product is avoided;

(d) Off-colors in the finished product can be avoided by the use of starting materials substantially free of heavy metal impurities which form colored sulfides;

(e) The use of the dangerous and noisome hydrogen sulfide gas as well as all of the equipment, cylinders, measuring devices, safety precautions, etc., required in previous methods is entirely obviated; and

(f) An inexpensive product of high depilating effectiveness is obtained.

The other components of the cream depilatories of the present invention are: (a) a filling agent or diluent, (b) a bodying and bonding agent and (c) optionally, a perfuming agent.

The filling agents or diluents may be chosen from among the chemically inert products well known and widely used for this purpose in the formulation of cosmetics. These include calcium carbonate (precipitated chalk), finely divided silica, strontium carbonate, barium sulfate, lithopone, gypsum, talcum, kaolin, magnesium carbonate magnesium oxide, kieselguhr, zinc oxide, bentonite, titanium dioxide, magnesium trisilicate, etc. All of these agents are stable, inert to the components of the depilatory at the pH of the product, inexpensive and readily available.

Evans (British Patent 451,611) has shown that the nature of the filler or diluent has a considerable effect on the time required to obtain effective depilation with strontium sulfide. I have also found that the use of calcium carbonate (precipitated chalk) as a filling agent in the products of the present invention produces a quicker and more effective depilating product than any other agent. This is highly advantageous since calcium carbonate is freely available in a state of uniformly great purity and at a low cost. It is therefore the preferred filling agent in these products.

The bodying and bonding agent may be chosen from among the following products: fatty alcohols, such as cetyl, lauryl, stearyl, etc., soaps such as sodium stearate, sodium myristate, etc., bentonite, cellulose ethers such as methyl cellulose, sodium cellulose glycolate (sodium carboxymethylcellulose), silica gel, alumina gel, etc., etc. In general, these bonding and bodying agents must be inert to the reducing agents in the

depilatory, indefinitely stable at a pH of 12 to 13 and capable of being frozen and thawed a number of times without "breaking." Perhaps the best of these is methyl cellulose, which is the preferred bodying and bonding agent for the products of the present invention.

The perfuming agents must be chosen very carefully in the light of the high reactivity of calcium hydrosulfide with many reducible organic compounds often used in the formulation of perfumes. Nitro compounds, such as the synthetic musks, are therefore counterindicated. The high alkalinity of the preparation (pH 12-13) makes it inadvisable to use the readily saponifiable esters or readily aldolizable aldehydes. The presence of the $-SH$ grouping may further cause certain alcohols to be converted to malodorous mercaptans.

In general, the best perfuming agents for products of this nature are based on terpenes and other hydrocarbons, some types of unreactive alcohols, ethers, ketones and on such specific perfuming agents such as the oils of vetiver, patchouli, thyme, lavender, lemon, citronella, cedarleaf, caraway, sandalwood and petitgrain and on synthetics such as ionone, safrole, vanillin, menthol, diphenylmethane, diphenyl oxide, betanaphthyl methyl ether, methyl acetophenone, isoamyl benzyl ether, terpineol, anethol, geraniol, etc., etc.

The concentrations of filling agent, bodying and bonding agent and perfume are so chosen as to give the finished depilatory formulation the proper consistency and texture. The finished product may be dispensed in tubes, jars, tins or in any convenient container the coating of which is not reactive with the components of the depilatory.

The products of the present invention will effect a safe and complete depilation when allowed to remain on the area to be dehaired for four to ten minutes, and usually in from four to five minutes. They are non-toxic, devoid of irritating effects and completely safe to employ.

The following example describes a typical depilatory composition of the present invention and the process of preparing the same. It is given by way of illustration and is not intended to limit this invention to reagents, proportions or conditions described therein. Obvious improvements will occur to any person skilled in the art.

Example

50.0 grams of sodium sulfide flakes, iron-free, assaying 60%-61% of Na_2S (0.385 mole) is dissolved in 375.0 c. c. of cold distilled water. At the same time, 60.0 grams of calcium chloride, technical flakes, assaying 75%-77% of $CaCl_2$ (0.405 mole) is dissolved in 90.0 c. c. of cold, distilled water. The calcium chloride solution is added with constant stirring to the sodium sulfide solution, whereby a uniform mixture is obtained. A total of 275.0 grams of lightweight, cosmetic grade precipitated chalk (calcium carbonate) is now added in small portions to the well-stirred mixture, care being taken to wet each portion of the precipitated chalk before the next is added. After all the precipitated chalk has been stirred into the mixture, there is added 150.0 grams of a 10% (weight-for-weight) gel of methyl cellulose (400 centipoise viscosity) in water, and the mixing is continued for at least thirty minutes or until a completely uniform, homogeneous cream is obtained. Five to twenty grams of a suitable perfume oil is now added, and

the mixture is stirred for another twenty to thirty minutes until completely smooth and uniform.

The resultant ivory to light grey colored cream depilatory may then be packaged in tubes, jars or tins, as desired. It will remain stable and effective when stored for prolonged periods of time under the usual conditions of shelf life.

This product is used in the manner usually employed with cream depilatories. The area to be depilated is covered with the preparation to a depth of 1 to 3 millimeters. For light hair, four to five minutes usually suffice; medium hair may require five to six minutes and coarse hair may require six to eight minutes of application of this product. At the end of this period, the depilatory paste is taken off by washing or by gentle mechanical removal and the depilated area is washed thoroughly with water until completely clean and devoid of remnants of hair or depilatory.

Having described my invention, what I claim and desire to protect by Letters Patent is:

1. A process for the manufacture of a cream depilatory which comprises mixing, per kilogram of finished product, 0.08 to 1.50 gram-moles of a water-soluble sulfide, at least an equimolar concentration of a water-soluble calcium salt and sufficient quantities of a filling agent, a bodying and bonding agent and a perfuming agent, to comprise the difference.

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2. A cream depilatory comprising a homogeneous mixture of (a) 50.0 grams of 60% sodium sulfide dissolved in 375.0 c. c. of water, (b) 60.0 grams of 75% calcium chloride dissolved in 90.0 c. c. of water, (c) 275.0 grams of calcium carbonate, (d) 150.0 grams of 10% gel of methyl cellulose (400 centipoise viscosity) and (e) 5.0 to 20.0 grams of a perfume oil.

JONAS KAMLET.

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The following references are of record in the file of this patent:

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