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EXOTHERMIC COSMETIC

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ABSTRACT OF THE DISCLOSURE

A packaged self-heating cosmetic, such as a shaving cream, includes separate exothermically reactive sulfinic acid or sulfinate reductant and an oxidant, which converts the reductant to the corresponding sulfonic acid or sulfonate, which serves as a surface-active ingredient of the heated cosmetic. Means are provided for dispensing the packaged reductant and oxidant and mixing them together so that they react and heat shaving cream or other cosmetic product constituents with which the exothermic reaction mixture is brought into contact. Preferably, the reducing agent employed is a metallic or non-metallic salt of benzene sulfinic acid or alkyl benzene sulfinic acid and the oxidizing agent is an aqueous solution of hydrogen peroxide.

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Heated cosmetics have been known to the art and for certain applications, as in shaving creams, they have been known to be more effective than cold products, especially in their ability to more rapidly soften the hairs of a beard and to prepare the beard for a close shave In recent years pressurized shaving cream, dispensed from so-called "aerosol" cans, have allowed the user to apply an already prepared lather, thereby saving the time and effort which was previously needed to work up a lather with shaving soap and brush. Such instant lathers have usually been dispensed at room temperature or at a slightly lower temperature, loss of heat content being due to vaporization or some of the more volatile components of the lathers as the pressure of the composition is reduced to atmospheric. Attachments have been made for pressurized dispensers so that the lather discharged therefrom will be electrically or mechanically heated but most of these devices are unwieldy, inefficient and comparatively expensive. Thus, self-heating cosmetic preparations, wherein the product dispensed from its container is heated by chemical reaction, are desirable products and research has been conducted in efforts to prepare commercially acceptable ones.

It has been known to dispense two fluids simultaneuosly from a pressurized container and it has also been known that by reacting together an oxidant and a reductant, heat will often be generated. It is also recognized that pressurized solutions of hydrogen peroxide will release oxygen when the pressure is reduced. Finally, it has been reported that sufinates can be converted to sulfonates by reaction with oxidizing agents. In such a reaction the sulfonate produced will foam, if it is in an aqueous medium. Although the reaction of sulfinate with oxidant is not new and the art recognized the need for exothermic cosmetics, before the present invention it was not suggested to employ an organic sulfinic acid or sulfinate in a reaction with an oxidant in the presence of cosmetic composition ingredients so as to dispense a heated cosmetic. The advantages of such a process and preparation were not disclosed. Included among such advantages are the additions to the final cosmetic of a surface active agent and water, as useful constituents thereof, resulting from the heating reaction, with the production of no undesirable byproducts.

In accordance with the present invention a self-heating cosmetic, such as a pressurized foaming shaving cream, is made by reacting and contacting with other cosmetic composition ingredients, an oxidizing agent and an organic sulfinic acid or sulfinate in a reaction which generates heat and produces a surface active organic sulfonic acid or sulfonate, whereby a heated cosmetic, such as a shaving cream in foamed form, is produced, which includes as a useful constituent, surface active organic sulfonic acid or sulfonate made by the exothermic reaction.

The invented process may be carried out by means of an container or suitable package or a combination of containers in which there are stored separately the oxidant and reductant and which includes means for simultaneously discharging both oxidant and reductant from their separate sources or compartments into contact with each other and other constituents of a shaving cream or other cosmetic preparation. The reaction heats the cosmetic while it is being dispensed. In preferred embodiments of the invention the oxidizing agent is a chemical such as hydrogen peroxide, in aqueous solution, preferably containing a stabilizing agent for the peroxide, and the reductant is an alkyl-, aryl-, or alkyl aryl sulfinic acid or corresponding salt. It is preferred to store the oxidant separately from the other cosmetic or shaving cream ingredients and it is similarly preferred to store the sulfinic acid or sulfinate reductant with the other ingredients.

Plural compartment pressurized dispensers are known and are in commercial use. Usually, a single container includes a main compartment which contains liquefied gas and other ingredients, plus a smaller compartment, which is collapsible, a valve or a plurality of valves communicates with the contents of the compartments via dip tubes or equivalent connections so as to allow simultaneous, joint dispensing of the contents, when desired. The valve or valves may be actuated by depression of a spout member, in which the contents of the compartments are mixed and from which they are discharged to the consumer. One such dispenser is illustrated in U.S. Pat. 3,325,056, although it is preferred to employ a design wherein the mixing of the components of the exothermic cosmetic occurs externally of the container, in the spout. Another apparatus that may be utilized for producing the heated cosmetic is illustrated in U.S. patent application S.N. 560,299, filed June 24, 1966 by Alan Dillarstone, wherein two dispensers, each containing one of two materials to be dispensed together, are joined and operated concurrently, discharging a mixture of materials through a common spout.

As the oxidant and reductant are mixed, they react to generate heat and warm the cosmetic in which they are incorporated. By employment of stoichiometric proportion of reductant and oxidant optimum heat will be generated but it is sometimes desired to speed the reaction by using an excess of one of the reactants, usually the oxidizing agent. With a particular cosmetic or shaving cream composition being dispensed, orifices and passageways of the valve parts may be so designed to provide the desired proportions of reactant materials. Where it is considered to be useful for the consumer to have some control of the temperature to which the cosmetic is raised by the exothermic reaction, the dispensing valves for plural compartments may be independently actuated, at least to an extent, so that the proportions of reactants may be altered, allowing more or less heat to be generated, depending on the ratios of oxidant and reductant compositions being dispensed. The temperature to which the cosmetic is raised will usually be controlled by the valve design or the user so that it does not become unbearably hot; the maximum temperature at which dispensing will usually occur is from 140° F. to 160° F. and will rarely

exceed 150° F. The permitted rise in temperature of the cosmetic over room temperature will usually be less than 10° F. and most often will be about 60 to 80° F. The heating will ordinarily raise the temperature of the cosmetic at least about 30° F. and the minimum temperature at which the heated cosmetic is dispensed will be about 100° F., although most products will be heated to at least 120° F. However, it is within the scope of the present disclosure to employ other dispensing temperatures, under appropriate circumstances.

The organic sulfinates or sulfinic acids of this invention are of the formula RSO_2M, wherein R is hydrocarbyl or substituted hydrocarbyl, preferably alkyl, aryl or alkyl aryl, and M is either hydrogen or a salt-forming cation. The aliphatic hydrocarbyl groups, which may contain up to 26 carbon atoms and usually up to 20 carbon atoms, for best performance, are preferably saturated and of straight chain structure, although alkyl groups thereof may also be branched. In the compounds wherein the sulfur of the sulfinate radical is joined to an alkyl the joining is preferably at a primary or secondary carbon atom, although linkage to a tertiary carbon is also useful. For the aromatic compounds the sulfur is preferably joined to a benzene ring, although it may also be substituted onto a naphthalene or other aromatic nucleus. The aromatic nuclei may have joined to them alkyl groups of 1 to 20 carbon atoms, preferably attached to a benzene ring either at the end or near the end of the alkyl chain, usually no more than three carbon atoms removed therefrom. Such an alkyl group will preferably be located para to the sulfur of the sulfinate or sulfinic acid.

Although both aliphatic and aromatic sulfinic acids and sulfinates are within the scope of the present invention, the aromatic compounds are preferred and the salts thereof are preferred to the free acids because of greater compatibilities with cosmetic constituents, better utilities of the corresponding sulfonates as components of the cosmetics, improved stabilities and greater solubilities in the cosmetics. The alkali metal and alkanolamine salts of benzene sulfinic acid and alkyl benzene sulfinic acids are especially preferred.

In addition to generating heat rapidly and efficiently when reacted with hydrogen peroxide or other suitable oxidants, the salts of benzene sulfinic acid and lower alkyl benzene sulfinic acid, such as those containing 1 to 3 carbon atoms in an alkyl side chain, impart a hydrotropic effect to the cosmetic composition upon oxidation of the sulfinate to sulfonate. Thereby, the cosmetic is improved by the hydrotrope solubilizing various constituents thereof and improving wetting action. Alkali metal and organic salts, particularly the potassium and ammonium salts of benzene sulfonic acid and lower alkyl benzene sulfonic acids are used widely in cosmetic and detergent products to aid in the production of homogeneous and fluid compositions.

On supplementing or if desired, replacing entirely the benzene sulfinate or lower alkyl benzene sulfinate with a higher alkyl benzene sulfinate, preferably of 10 to 16 carbon atoms in the alkyl chain, the heat-generating action is accompanied with the production of long chain alkyl benzene sulfonates, which are known to be excellent detergents and are often desirable constituents of cosmetics for their detersive and surface active properties. The higher alkyl sulfinates, of 10 to 16 carbon atoms may also be used for similar purposes, since they are converted to the corresponding alkyl sulfonate detergents.

The aromatic sulfinic acids and sulfinates may be alkylated or polyalkylated and may contain other non-interfering or compatible substituents. Among suitable substituents are lower alkoxy groups of 1 to 4 carbon atoms, all the halogens, hydroxy, sulfonic, carboxy and other compatible groups. Usually, only one each substituent will be employed and that will ordinarily be on the aryl group, but up to three substituents may be present and they may be the same or different.

The salt-forming cations may be any such suitable ion but will preferably be one that is usually found in cosmetic preparations. Ammonium or alkylolamine are preferred but alkali metal and other metal salt-forming ions may also be used. When accompanied by other constituents of a shaving preparation, sulfinate will usually be present, rather than the sulfinic acid, because of the alkalinity of the shaving preparation. Among suitable alkylolamines that may be used are triethanolamine, diethanolamine, ethanolamine, triisopropanolamine, isopropanolamine, diisopropanolamine, N-methyl diethanolamine, N,N-dimethylethanolamine, N-methyl ethanolamine, N-ethyl diisopropanolamine, N,N - diethyl n-butanolamine, and other lower alkanolamines having from 1 to 3 alkanolamine groups of 1 to 4 carbon atoms per alkanol. The alkyls of the alkanol groups may be substituted by non-interfering radicals, such as halogens, lower alkoxy or other similar substituent. Alkali metal salts are also useful sulfinates, including the sodium, potassium and lithium salts. Alkaline earth metal salts, zinc, tin, magnesium and aluminum sulfinates may be used, when suitable in the formula being dispensed. In short, any non-interfering metal or other salt-forming cation may be employed to make a suitable sulfinate, as long as it possesses sufficient solubility. By non-interfering it is meant that it does not prevent the oxidation-reduction reaction or significantly adversely affect the chemical, physical or aesthetic properties of the cosmetic being dispensed. In this respect, it will be noted that the preferred ammonium and alkylolamine salts are milder to the skin than many of the metallic salts, although where mildness is not an important consideration the metal salts can be used equally well.

The sulfinic acid reductants are stronger acids than the carboxylic acids. They form stable salts, which may crystallize with water of hydration. The aromatic sulfinic acid compounds are usually of greater stability than the aliphatic analogues, and the salts are more stable than the acids. Sulfinic acids are most frequently prepared by the action of a reducing agent, such as zinc or sodium sulfite, on a sulfonyl halide, such as a chloride or a bromide, in neutral or basic aqueous or alcoholic medium. They may also be prepared from Grignard reagents and sulfur dioxide. Of course, the products made are convertible to either the acid or salt form by treatment with acid or base, as the case may be. Methods of preparation which are adaptable to produce the sulfinic acids and sulfinates of this invention are described in Chemical Review, vol. 48, pages 69–124 (1951) by W. E. Truce and A. M. Murphey and in the Journal of Organic Chemistry, vol. 7, pages 23–30 (1942) by P. Allen, Jr.

As examples of sulfinates that may be used in accordance with this invention there are listed the following:

Sodium ethanesulfinate;
magnesium butanesulfinate;
sodium 1-dodecanesulfinate;
potassium 1-pentadecanesulfinate;
triethanolamine propanesulfinate;
ammonium 1-tetradecanesulfinate;
sodium benzene-sulfinate;
ethanolamine benzenesulfinate;
triethanolamine paratoluenesulfinate;
potassium para-toluenesulfinate;
methylamino ethanol benzenesulfinate;
methyl diethanolamine ortho-toluenesulfinate;
sodium para-chlorobenzenesulfinate;
lithium ortho-toluenesulfinate;
potassium para-methoxybenzenesulfinate;
diethanolamine para- (1-methylethyl)-benzenesulfinate;
lithium meta-dodecylbenzenesulfinate;
potassium paradodecylbenzenesulfinate;
sodium para-dodecylbenzenesulfinate;
triethanol amine para-dodecylbenzenesulfinate;
sodium 1-chloronaphthalene-6-sulfinate; and
ethyl diisopropanolamine para-propylbenzenesulfinate;

and the corresponding free acids.

The oxidizing agent which may be reacted with the sulfinic acid or sulfinate may be any of such materials which is capable of converting the sulfinate to sulfonate, with the evolution of sufficient heat to warm appreciably the cosmetic being dispensed. Although various organic oxidants may be used, it is preferred to employ per-compounds to convert the sulfinates to sulfonates. For simplicity, when sulfinate and sulfonate are recited herein the terms include the corresponding acids, too. Among the per-compounds, the inorganics are preferred, especially those which are converted to innocuous or helpful byproducts by the oxidation reaction. Among the most preferred is hydrogen peroxide, preferably in aqueous solution, but sodium peroxide, sodium perborate, potassium percarbonate, sodium persulfate and urea hydrogen peroxide find use, too. Thus, alkali metal, alkaline earth metal and other metal per-compounds and compounds which provide hydrogen peroxide for the present reactions are oxidants contemplated as within this invention. To obtain special properties, mixtures of the oxidants may be used.

Although many different oxidizing agents may be used to convert the sulfinate to sulfonate and generate heat to warm the cosmetic composition, it has been found to be most preferable to use hydrogen peroxide, preferably in a stabilized aqueous solution, as will be observed, the by-products from hydrogen peroxide are limited to water if the oxygen is consumed in converting the sulfinate to sulfonate. Water is a normal constituent of cosmetic compositions and shaving creams and does not add irritating cations or other interfering ions to the product.

It is preferred to employ the oxidizing agent as a separate aqueous solution, apart from the other cosmetic and reducing agent constituents of the cosmetic preparations. Various concentrations of oxidant in water may be used, usually from 3 to 30% by weight. When hydrogen peroxide is used, so as to maintain container size as small as possible and to promote efficiency in the heat-generating reaction, there should be employed from 5 to 30%, preferably 8 to 15% and most preferably, from 9 to 12% hydrogen peroxide in aqueous solution. Minor amounts of sequestrants, chelating agents or other stabilizers, such as nitrilotriacetic acid or its trisodium salt, ethylene diamine tetraacetic acid or salt thereof, stannic chloride, silicates or other known compounds for stabilizing purposes may be present with the hydrogen peroxide.

The oxidizing action of the hydrogen peroxide is increased considerably by the presence of metal catalysts. Thus, tungstates, molybdates and uranates and other salts and catalytic materials for releasing active oxygen from the per-compound or promoting its activity may be used to increase the reaction efficiency of a redox system employing hydrogen peroxide as the oxidant. Usually the alkali metal or ammonium salts are used, e.g., ammonium molybdate, potassium tungstate, sodium uranate. Because metals that activate hydrogen peroxide systems might also act to convert the hydrogen peroxide to a less stable form, in accord with the present invention the catalyst will usually be incorporated in the zone containing the sulfinate and will not contact the stabilized hydrogen peroxide until such time as the reaction between reductant and oxidant is to be effected.

The other constituents of the cosmetic compositions are those known to the art to impart the desired cosmetic properties for the particular purpose. Most cosmetics and shaving preparations include hydrophilic and lipophilic components, usually in their respective phases, together with an emulsifying or wetting agent to help form a stable emulsion. For example, in a hand cream the lipophilic phase can include lanolin, mineral oil, stearic acid, petrolatum, animal fats, vegetable and petroleum waxes and emollients, while the aqueous phase may contain water, glycerol, other solvents and buffers, with soaps or synthetic organic emulsifiers to produce and maintain the emulsion. Correspondingly, in hair-removing preparations, the active depilatory may be present in either phase, although it is usually water soluble and therefore, is found in the aqueous phase, for the most part. In some cases, instead of employing emulsions, solutions of an ingredient may be used. Material dispensed may be in liquid, paste, gel or preferably, in foam form. The foams are created by the action of a dissolved pressurized or liquefied gas dispersed through the composition, which is released as a gas and expands the composition.

In shaving preparations, the shaving emulsion dispensed from one compartment of a pressurized container comprises a major proportion, up to about 95% of water, and the rest of the material includes soap or other beard softeners, solvents, emulsifying and conditioning agents. The soap is preferably a stearic acid soap, made from commercial double or triple pressed stearic acid. However, other higher fatty acid soaps, such as those of tallow, corn oil, cottonseed oil, animal greases and other animal fats and vegetable oils may be employed. Usually however, a major proportion of the soap-forming fatty acid of the soap should be of 16 to 18 carbon atoms. The cation of the soap is preferably an alkanolamine, such as triethanolamine, although other tri-, di- and monoalkanolamines of 1 to 4 carbon atoms per alkyl group are useful. If desired, alkali metal soaps, such as sodium and potassium soaps may be employed, as may be ammonium and lower alkyl amine soaps. For best results in producing a soap which does not irritate the skin after shaving and which is fluid enough so as to be dispensed entirely from the container a triethanolamine soap is used, together with minor proportions of sodium and potassium soaps to stabilize the lather. Where superfatting effects are desired, the fatty acid employed may be only partly neutralized by the cation of neutralizing agent, leaving the free fatty acid present to exert its emollient effect upon the skin.

Alkylolamides also have a conditioning effect on the hair and skin, in addition to stabilizing foams of cosmetic compositions. Included in the alkylolamide group are dialkylolamides, such as lauricmyristic diethanolamide, and other alkylolamides wherein the acyl groups are of 12 to 18 carbon atoms, preferably with 50% by weight or more being of 12 to 14 carbon atoms. The alkylol groups are preferably of 1 ot 3 carbon atoms each.

As emollients or solvents it is preferred to employ polyhydric alcohols of 3 to 6 carbon atoms per molecule, having 3 to 6 free hydroxyls per molecule. Exemplary of such compounds are glycerol and sorbitol, although other alcohols such as pentaerythritol, mannitol and other sugar alcohols are also used.

Various suitable emulsifying or surface active agents may be important igredients of the present products and these include the anionic, cationic and nonionic compounds. Of these materials it is preferred to use the nonionics and of these the most preferable group is that of the higher ethers of ethoxylated alkyl phenols and of higher fatty alcohols. These compounds, known commercially as Igepals, a trademark of GAF Corporation, usually have an alkyl group of 6 to 10 carbon atoms on the phenol ring and the degree of ethoxylation is from 1 to 50 ethoxy groups per molecule, with the higher fatty alcohol being of 10 to 18 carbon atoms per molecule, usually averaging about 12 carbon atoms. Other nonionic compounds, such as esters of higher fatty acids and ethoxylated alcohols, condensates of groups of higher ethylene oxide polymers and higher propylene oxide polymers, and esters of ethoxylated fatty acids and sugar alcohols or hexitane are representative of the nonionics that may be included in the present formulations. Among the anionic surface active agents are the higher alkyl sulfates and alkyl sulfonates, the higher alkyl benzene sulfonates, ethoxylated fatty alcohol sulfates, monoglyceride sulfates, higher fatty acid amides of amines, such as sodium lauroyl sarcoside, phosphates corresponding to the above-mentioned sulfates, and sulfates and sulfonates of the mentioned nonionic compounds, where possible. Among the cationic surface

active agents may be mentioned the quaternary ammonium and phosphonium compounds, e.g., trimethyl benzyl ammonium chloride, cetyl trimethyl ammonium bromide and lauryl pyridinium chloride, all of which exert antiseptic, as well as surface activity.

In self-pressurized "aerosol" compositions a liquefied gas, such as a lower hydrocarbon or a lower halogenated hydrocarbon, may be employed to aid in discharging the oxidant and reductant portions of the cosmetic preparation. Especially when the liquefied gas is emulsified into one or both of the portions of the cosmetic, it will assist in generating a foam as the liquefied propellant is converted to minute gas bubbles. If it is desired to use only water and hydrogen peroxide or other oxidant therein, instead of liquefied hydrocarbon or liquefied halogenated hydrocarbon, compressed nitrogen, carbon dioxide, oxygen or other non-liquefied gas may be used, to provide the force to discharge the oxidant material. Among the liquefied gas propellants which may be employed are the lower hydrocarbons of 3 or 4 carbon atoms, which include n-butane, isobutane and propane, preferably employed as a mitxure of isobutane and propane, preferably 85 to 90 parts isobutane and 10 to 15 parts propane. The halogenated hydrocarbons are preferably those which are at least partially fluorinated, including monochlorotrifluoromethane, dichlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, monochloropentafluoroethane, trichloromonofluoromethane, tetrachlorodifluoroethane, and similar chlorofluorohydrocarbons, having 1 ot 3 carbon atoms per molecule. Of course, mixtures of the halogenated hydrocarbons are also employed, desirably to regulate the pressure developed, solubilizing properties, corrosion prevention, emulsion formation, and so forth. In some instances it may be desirable to utilize completely chlorinated or fluorinated hydrocarbons as propellants or diluents, e.g., methylene chloride, where they are acceptable.

All cosmetic compositions contain adjuvant materials to make the product aesthetically acceptable or specially appealing. Perfumes, dyes, pigments, emollients, solvents, thickeners, solubilizers, humectants, buffers, antiseptics, foaming agents, preservatives and similar materials, generally in minor proportions, usually less than 5% each and preferably less than 2% each and most preferably less than 1% each, with the total thereof being less than 25%, preferably less than 10% and most preferably less than 5% of the composition, are often employed.

The proportions of various other constituents of the present compositions are regulated to a large extent by the type of composition being prepared. Usually for cosmetic compositions there will be present from 2 to 50% of the active cosmetic ingredient, although more or less may also be employed in special cases. There will also usually be employed from 5 to 90% solvent or dispersion medium and from 1 to 25% of surface active agent, which group includes soaps. In some circumstances, as in shaving creams, the active ingredient and the surface active agent may be the same, since one compound serves both functions. In pressurized compositions, there with usually be present from 3 to 90% of liquified or compressed gas. Of course, the given proportions apply to most cosmetics, but it must be realized that for certain compositions proportions outside the given ranges may also be acceptable, even preferred.

Pressurized shaving creams preferably contain from 50 to 75% water, more preferably 55 to 65%, 1 to 20% of synthetic organic surface active agent, exclusive of that produced by the redox reaction, preferably 1.5 to 4% thereof, or 10 to 40%, including such products, 5 to 20% soap, preferably 8 to 15% thereof, and 2 to 20% of humectant, such as glycerine or sorbitol, which may also exert a solvent action in the composition. Preferably, there is used from 3 to 10% of such humectant. In most compositions minor proportions of foaming agent and perfume, both usually within the range of 0.1 to 5% and preferably, from 0.3 to 1% are also often utilized. In heated shaving creams the soap solution will usually include from 10 to 35%, and preferably from 15 to 25% of organic sulfinate reactant, but the sulfinate may be separately dispensed, too. Together with the sulfinate or separately dispensed will often be present 0.2 to 2%, preferably 0.3 to 1% of molybdate or tungstate catalyst, or other suitable catalyst for the reaction in desirable amount. The hydrogen peroxide contained in the separate compartment to avoid premature contact with the reductant will usually be from 1.5 to 5% of the weight of the soap solution and will be present as an aqueous solution of from 3 to 30% strength. Thus, the hydrogen peroxide solution can be from 0.4 to 150% of the soap solution weight and is preferably about 20 to 30% thereof.

The pH of shaving preparations is normally regulated to be on the alkaline side and is preferably no higher than 10.5. Thus, it is preferable to employ compositions having a pH of 7 to 10, although those of pH from 5 to 11 may also be used, when desired for a particular type of application. The pH may be regulated by use of compatible buffers, such as acid-base, salt-base and acid-salt mixtures, e.g., including borates, phosphates, carbonates, sulfates or silicates, or other acceptable inorganic or organic salts, including salts of alkylolamines. The soap or soaps present in the shaving compositions may exert a buffering effect and may be the primary or even the sole buffers present.

The cosmetic preparations of this invention are made by simple methods known to the art. The various constituents of the cosmetic portion of the preparations themselves may be combined in the normal manner and then, depending on the nature of the cosmetic, may be further formulated with either the oxidizing agent or the reducing agent employed. If the cosmetic preparation is essentially oxidizing in nature, it will preferably be combined with the oxidizing agent. The reverse situation is also applicable and in most cases, the cosmetic will have the ingredients thereof packed together with the reductant and catalyst, with the oxidant being separately packaged, usually in a different compartment of the dispenser. If some of the constituents of the cosmetic are oxidizing and others are reducing by nature, the composition may be formulated by such parts and one part may accompany the heat-generating oxidant and the other may be stored with the reductant. The main consideration is that no unwanted oxidation-reduction should occur due to premature combination of a heat-generating chemical of this invention with a cosmetic ingredient. Of course, if so desired, the oxidizing agent and the sulfinate may be kept separate and not formulated with any other cosmetic component. In such situations, the cosmetic may be separately dispensed from a container and only brought into contact with the heat-generating chemicals upon discharge from the container. In such an arrangement a three-compartment container may be employed or three or other number of separate containers may be used in conjunction.

Self-heating cosmetic preparations of this invention include various compositions intended for application topically to the human body. Usually these are applied to the skin or hair. They include face creams, body lotions, depilatories, tanning agents, antiperspirants, sun-screens, personal deodorants, hair creams, hair lotions, hair gels, shampoos, dyes, bleaches, rinses, shaving creams make-up preparations, bath oils, facial treatments, astringents, after-shave lotions and many other related preparations. In most of these, organic sulfonate detergents, hydrotropes or other surface active agents are important or useful constituents, either as detergents, hydrotropes, emulsifiers or as contributors of desirable wetting or surface active properties. By the method of the present invention, such compounds are prepared in the dispensing of the cosmetic during the heating thereof and are immediately solubilized or dispersed in the cosmetic, partly due

to the heat generated in the exothermic reaction which produced them. The heat generated produces small currents in the cosmetic being dispensed which help to distribute the surface active sulfonate and by distributing the sulfonate throughout the composition, the ease of wetting the various areas of the cosmetic preparation is further increased. The heat generated also helps further to solubilize cosmetic preparation ingredients and thereby improves homogeneity of the product. This coaction between the surface active agent produced, the heat generated and the other cosmetic preparation ingredients is a useful result of the present invention and helps to avoid poorly dispersed ingredients or products of the exothermic reaction. The surface activity of the sulfonate made also helps to distribute throughout the cosmetic the water and other byproducts of the heating reaction and thereby effects a better and more even heating of the cosmetic. Thus, pockets of undispersed materials in the cosmetic are avoided and final product is uniform.

Among other advantages of the present invention are the reasonable costs of the oxidants and reductants and their low corrosivity toward ordinary materials of container construction, such as tinplate or steel coated with resins commonly used for that purpose. Thus, blockages of valve parts are not encountered, due to corrosion byproducts being released into the cosmetic being dispensed through the valve. In addition to low corrosive action, the present oxidants and reductants are remarkably compatible with normal cosmetic ingredients and do not form undesirable products that would adversely affect the cosmetic properties of the preparations. It is considered to be important in most cases that the products of the exothermic reaction are not gaseous, since the present systems are thereby made useful for liquids, emulsions and creams, as well as foams. Of course, by use of propellants, such as liquefied gases, emulsions may be dispensed as foams and liquids may be dispensed as sprays, when desired. Here again, it is important that the present exothermic compositions not change the foaming activity of the liquefied gases or other foaming agents, so that the foaming obtained can be pre-planned, being dependent on the ingredients of the composition used, without being affected by additional gases produced in the heating reactions. Thus, except for the expansion of the foam on heating, the regular tried and tested proportions of foaming agents or spraying agents may be used with the cosmetics. Of course, the heat expansion does increase foam volume and can help save propellant, to some extent.

The lack of gas production in this reaction is a protective feature of the invention because accidental rupturing of a sac containing a reactant will not result in gas generation. If it did, the pressure created could cause the container to explode. It has been found that the present exothermic reaction, even if initiated by sac leakage, will not cause such explosion.

Although all the above-mentioned properties are of importance in producing a satisfactory self-heated cosmetic, a most important property is low toxicity of the heat-generating chemicals. The present materials are low in toxicity and are completely suitable as ingredients in cosmetics. They are converted into sulfonated compounds which are well-known constituents of materials that have been employed safely in large tonnages in recent years, in detergents and in cosmetics. They are safe. Another very important property of cosmetics is a pleasing odor. The present materials are of low odor and are converted to sulfonates, which are practically odorless. Thus, the present compositions are aesthetically acceptable. This is important when it is considered that many other sulfur-containing reducing agents, such as thiourea, for instance, can be oxidized or otherwise converted to malodorous products, thereby making useless any cosmetic in which such reaction occurs.

The following examples illustrate some preferred compositions within the present invention. Of course, such examples are not to be considered as limiting the invention, because they are only exemplary thereof. Those of skill in the art will know how to replace various constituents and procedural steps of the invention with corresponding equivalent materials or operations without departing from the principles or teachings imparted herein. Unless otherwise stated, all parts given by weight.

EXAMPLE 1

	Parts (by weight)
Stearic acid (double pressed)	8.0
Sorbitol (70% active, aqueous solution)	5.0
Nonyl phenyl polyoxyethylene ethanol of 30 oxyethylene groups per mole (Igepal CO–880)	4.0
Triethanolamide	4.0
Water (deionized)	47.5
Sodium hydroxide (25% aqueous solution)	1.0
Triethanolamine toluene sulfinate 70% aqueous slution)	28.5
Perfume	.75
Ammonium molybdate (20% aqueous solution)	1.25

The stearic acid, sorbitol and nonionic surface active agent are mixed together and heated to 185° F. The triethanolamine and water are combined and heated to the same temperature, and then both of the portions are combined at 185° F. Next, the sodium hydroxide is added, with mixing. The emulsion resulting is cooled to 100° F. and the perfume, triethanolamine toluene sulfinate and ammonium molybdate are added, with mixing, after which the resulting perfumed emulsion is further cooled to 80° F. This portion of the cosmetic preparation, including all the cosmetic ingredients plus the reductant and catalyst for the redox reaction, is then added to the larger compartment of a plural compartment dispensing container. Then, 25 parts of an 11% aqueous solution of hydrogen peroxide, containing about 0.2% of phenacetin as a stabilizer, are filled into the smaller compartment or sac of the dispenser. Both compartments communicate with a dispensing valve or valves. The dispensing valve is then staked into place at the outlet of the dispensing container. 6.0 parts of propellant, in the gaseous state, are then pressure filled into the larger compartment, from which propellant pressure is exerted on the materials in both compartments. The hydrocarbon propellant is a mixture of 83.5% isobutane and 16.5% propane. The pressurized shaving cream is now ready for use.

The pressurized product made by the method of this example has an excellent shelf life. When the dispensing valve of its container is actuated the shaving cream dispensing is an effective softener for the beard and permits almost effortless, smooth and pleasant shaving. In part, this result is attributable to the temperature of the shaving cream dispensed, which rises to about 140° F. within thirty seconds after dispensing it with the oxidant and reductant from the container, at 70° F. The cream is pleasantly perfumed and there is no malodorous component evident.

Comparable results are obtained when the triethanolamine sulfinate of toluene is replaced by triethanolamine benzene sulfinate or triethanolamine xylene sulfinate or a mixture thereof. To obtain additional detersive and wetting action, triethanolamine dodecyl benzene sulfinate may be substituted for the other sulfinates, either in whole or in part, and a sumilarly effective product results. When the amount of peroxide is decreased to 13 parts, less heating is obtained and the temperature of the cream reaches only about 120° F. thirty seconds after dispensing.

When 4.5 parts of triethanolamine are employed instead of the 4.0 parts of the formula given above, and no sodium hydroxide is used, with the omitted ½ part made up by additions of ½ part water to the formula, a good self-heating shaving cream results with essentially the same properties as those described above. However, the

lather is more fluid and is not as firm or stable as that of the formula incorporating the small proportion of sodium soap. Similarly, when the sodium hydroxide is replaced with potassium hydroxide in stoichiometric proportion a firmer lather results than that from the triethanolamine soap alone. Reducing the hydrogen peroxide concentration to 10% does not significantly adversely affect either the temperature to which the lather is raised or the speed of heat generation.

When ammonium molybdate is replaced with alkali metal tungstate or molybdate, in these essentially triethanolamine soap formulas, catalytic action falls off. Apparently, it is desirable to have the cation of the catalyst the same as that of soap and sulfinate, or at least to have it contain nitrogen, as in ammonium, if the soap and sulfinate contain nitrogen.

All are good self-heating shave creams, being at a temperature of about 130 to 150° F. one minute after dispensing. The lather is not as thick as that of the product of Example 1.

When the proportion of propellant is changed so that from 3 to 10% by weight thereof is present, efficient dispensing is encountered over the range, with faster dispensing and greater foaming being obtained at the higher propellant ratios, as would be expected.

In similar experiments, wherein cetyl alcohol, glycerine or other humectants and emollients are added to the compositions made, little differences in heating properties or stabilities are found. When the ratios of catalyst are halved or doubled, heating times are affected somewhat. When excess peroxide, from 0.1 to 20 or 30% of the stoichiometric amount is used, the reaction is hastened but even with only the stoichiometric amount, it proceeds quickly and the shaving cream is ready for use soon.

When the base formula is replaced by a conventional foaming anionic shampoo, a foamable hair conditioner, or a sun-screening cosmetic containing foaming agent, the corresponding self-heating foaming product is dispensed correspondingly. When non-foaming materials such as facial emulsion, skin cream, or deodorant formulations, which may contain anti-foaming agents, are substituted for the base formula, non-foaming but surface active heated products are made.

EXAMPLES 2-9

	Parts by weight							
	2	3	4	5	6	7	8	9
Stearic acid (triple pressed)	6.3	6.3	4.0	5.6	4.0	6.3	4.0	6.3
C_{10}-C_{16} fatty acids (from coconut oil)	2.7	2.7	2.7	2.4	2.7	2.7	2.7	2.7
Light mineral oil			10.0				10.0	
Triethanolamine	4.6	4.6	3.0	17.4	12.0	4.6	3.0	4.6
Sorbitol (70% aqueous solution)	10.0	10.0	10.0	8.9	10.0	10.0	10.0	10.0
Water	75.9	75.9	69.8	67.5	41.3	65.9	69.8	65.9
Perfume	5.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Lanolin esters (Amerchol 101)						10.0		10.0
Potassium benzene sulfinate (45% aqueous solution)		37.5	37.5	37.5	26.5	37.5		
Sodium tungstate (10% aq. solution)	3.6	4.2	4.2	4.2	3.0	4.2	3.6	3.9
Hydrogen peroxide (11% aq. solution)	30.0	35.0	35.0	35.0	25.0	35.0	30.0	32.7
Propellant (5:1 mixture of isobutane and propane)	4.5	5.4	5.4	5.5	3.8	5.4	4.7	5.0
Triethanolamine toluene sulfinate (92.3% active)	17.5						17.5	28.2

Self-heating facial cleaner compositions of the formula given above in Examples 2–9 are made, following the general method of Example 1, modified for the present compositions by adding the coconut oil fatty acids and mineral oil or lanolin esters with the stearic acid and heating to 185° F., and then proceeding to prepare and fill the dispensers. All of the products are heated foaming cleanser cosmetics, with the temperatures to which they are raised being from 120° F. to 150° F. As is seen from the formulas, some are superfatted and some contain excess triethanolamine.

EXAMPLES 10–12

	Parts
Water	54.9
Stearic acid	7.7
Coconut oil fatty acids	1.0
Lauric myristic diethanolamide	1.0
Triethanolamine	4.8
Perfume	.75

To the above base formulation are added the following to make the products of Examples 10–12, respectively:

EXAMPLE 10

	Parts
Base formula	99.6
Triethanolamine toluene sulfinate (92.3% active)	31.0
Sodium tungstate dihydrate (11.3% aq. sol'n.)	4.4

EXAMPLE 11

	Parts
Base formula	105.5
Potassium toluene sulfinate (49.4% active)	38.0
Sodium tungstate (10.0% active aq. sol'n.)	1.5

EXAMPLE 12

	Parts
Base formula	99.0
Potassium benzene sulfinate (45.4% active aq. sol'n.)	41.6
Sodium tungstate (10% active aq. sol'n.)	4.4

The above formulations are prepared as in Example 1 and are filled into dispensing containers with 36 parts of an 11% aqueous hydrogen peroxide solution in a separate zone and with 5.5 parts of the propellant of Example 1.

EXAMPLES 13–15

	Parts
Water	46.6
Stearic acid	7.7
Coconut oil fatty acids	1.0
Lauric myristic diethanolamide	0.5
Cetyl alcohol	0.5
Triethanolamine	10.0
Potassium hydroxide (34.2% aq. soln.)	3.0
Perfume	0.8

To the above formulation are added the following to make the products of Examples 13–15.

EXAMPLE 13

	Parts
Base formula	99.0
Potassium benzene sulfinate (45.4% aq. soln.)	41.6
Sodium tungstate (10% aq. soln.)	4.4

EXAMPLE 14

	Parts
Base formula	104.4
Triethanolamine toluene sulfinate (76.3% aq. soln.)	36.3
Sodium tungstate (10% aq. soln.)	4.4

EXAMPLE 15

	Parts
Base formula	105.5
Potassium toluene sulfinate (49.4% aq. soln.)	38.0
Sodium tungstate (10% aq. soln.)	1.5

The above formulations are prepared in the manner described for Examples 10–12 and are filled into dual compartment dispensing containers with six parts of the

propellant of Example 1 and 36 parts of 11% aqueous hydrogen peroxide. The products dispensed are good shaving creams, with that of Example 14 being rated milder to the face. The cream of Example 13 is thicker than that of Example 15. All heat to 120 to 150° F. in 10 to 60 seconds.

When other active ingredients are added to those formulas, such as dyes, skin conditioners, bactericides, fungicides, compatible bleaches, etc., the products are uesful in performing the cosmetic functions of such additives.

What is claimed is:

1. A self-heating cosmetic product comprising constituents stored in separate zones of a container or containers in one of which zones there is present from about 10–35 percent by weight of an organic sulfinic acid or sulfinate reductant of the formula RSO_2M, wherein R is an unsubstituted or substituted hydrocarbyl selected from the group consisting of alkyl of 10 to 16 carbon atoms, phenyl, lower alkylphenyl wherein the lower alkyl is of 1 to 3 carbon atoms, and higher alkylphenyl in which the higher alkyl is of 10 to 16 carbon atoms, the substituents being selected from the group consisting of lower alkoxies carboxyl, with from 1 to 3 thereof being present, and M is hydrogen or a salt-forming cation selected from the group consisting of ammonium, lower alkanolamine of 1 to 3 alkanol groups and 1 to 4 carbon atoms per alkanol group, alkali metals, alkaline earth metals, zinc, tin, magnesium and aluminum, and in another of which zones there is present at least about the stoichiometric amount of an oxidizing agent for reaction with said reductant, said oxidizing agent being selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, alkali metal peroxide, alkali metal perborate, alkali metal percarbonate, alkali metal persulfate, alkaline earth metal peroxide, alkaline earth metal perborate, alkaline earth metal percarbonate and alkaline earth metal persulfate, said oxidizing agent being exothermically reactive with the reductant to convert it to a surface active organic sulfonic acid or sulfonate and simultaneously to heat the product when dispensed, and from about 3–90 percent by weight of a pressurized gas in at least one of the zones and means for dispensing contents from both zones simultaneously and into contact with each other, whereby there is produced by exothermic reaction of the sulfinic acid or sulfinate and the oxidizing agent a heated cosmetic preparation including therein the organic sulfonic acid or sulfonate produced, as a surface active constituent thereof.

2. A product according to claim **1** wherein the reductant is an alkali metal phenyl sulfinate or alkali metal alkylphenyl sulfinate wherein the alkyl is of 1 to 3 or 10 to 16 carbon atoms, and the oxidizing agent is aqueous hydrogen peroxide.

3. The product of claim **1** wherein said product additionally contains from about 2–50 percent by weight of a soap selected from the group consisting of lower alkanolamine, ammonium, and alkali metal soaps of fatty acids in which a major proportion of the fatty acid content is of 16–18 carbon atoms and wherein said alkanolamine has from 1–4 carbon atoms per alkyl group.

4. A product according to claim **3** wherein the cosmetic is a cleanser composition.

5. A self-heating aqueous shaving cream product comprising constituents stored in separate zones of a container in one of which zones there is present from about 10–35 percent by weight of an organic sulfinic acid or sulfinate reductant of the formula RSO_2M, wherein R is an unsubstituted or substituted hydrocarbyl selected from the group consisting of alkyl of 10 to 16 carbon atoms, phenyl, lower alkylphenyl wherein the lower alkyl is of 1 to 3 carbon atoms, and higher alkylphenyl in which the higher alkyl is of 10 to 16 carbon atoms, the substituents being selected from the group consisting of lower alkoxies of 1 to 4 carbon atoms, halogens, hydroxy, sulfonic, and carboxy, with from 1 to 3 thereof being present, and M is hydrogen or a salt-forming cation selected from the group consisting of ammonium, lower alkanolamine of 1 to 3 alkanol groups and 1 to 4 carbon atoms per alkanol group, alkali metals, alkaline earth metals, zinc, tin, magnesium and aluminum, and in another of which zones there is present at least about the stoichiometric amount of an oxidizing agent for reaction with said reductant, said oxidizing agent being selected from the group consisting hydrogen peroxide, urea hydrogen peroxide, alkali metal peroxide, alkali metal perborate, alkali metal percarbonate, alkali metal persulfate, alkaline earth metal peroxide, alkaline earth metal perborate, alkaline earth metal percarbonate and alkaline earth metal persulfate, said oxidizing agent being exothermically reactive with the reductant to convert it to a surface active organic sulfonic acid or sulfonate and simultaneously to heat the shaving cream when dispensed, and from about 3–90 percent by weight of a pressurized gas in at least one of the zones and valve means for dispensing contents from both zones, with the aid of the pressure of the pressurized gas, simultaneously and into contact with each other, whereby there is produced by the exothermic reaction of the sulfinic acid or sulfinate and the oxidizing agent a heated cosmetic preparation including therein the organic sulfonic acid or sulfonate produced, as a surface active constituent thereof.

6. The product of claim **5** wherein said product additionally contains from about 2–50 percent by weight of a soap selected from the group consisting of lower alkanolamine, ammonium, and alkali metal soaps of fatty acids in which a major proportion of the fatty acid content is of 16–18 carbon atoms and wherein said alkanolamine has from 1–4 carbon atoms per alkyl group.

7. A shaving cream product according to claim **6** wherein the oxidizing agent is aqueous hydrogen peroxide, and the product, before dispensing, is in two separate compartments of a valved dispensing container, and a solution comprising said sulfinic acid or sulfinate, said higher fatty acid soap and water are in one compartment and said oxidizing agent is in the other, said solution including 10 to 35% of the sulfinic acid or sulfinate, the hydrogen peroxide being 1.5 to 5% of the weight of said solution, and the final product, after dispensing, comprising 5 to 20% soap and 50 to 75% water and being at a pH of 5 to 11.

8. A shaving cream according to claim **5** wherein the reductant is an alkali metal phenyl sulfinate or alkali metal alkylphenyl sulfinate wherein the alkyl is of 1 to 3 or 10 to 16 carbon atoms, and the oxidizing agent is aqueous hydrogen peroxide.

9. A shaving cream according to claim **8** wherein there is present with the reductant a catalyst for the redox reaction, selected from the group consisting of alkali metal and ammonium tungstates, molybdates, and uranates, in an effective amount to accelerate the exothermic reaction and to heat the cosmetic product to a temperature of 100° F. or more within 30 seconds after dispensing.

10. A shaving cream product according to claim **7** wherein the reductant is an organic sulfinate, the soap solution contains from 0.2 to 2% of an alkali metal or ammonium molybdate, tungstate or uranate catalyst for the redox reaction, the soap of the soap solution is a mixture of triethanolamine soap and alkali metal soap with the triethanolamine soap being over 50% of the soap content and the pressurized gas is a mixture of lower hydrocarbons of 3 to 4 carbon atoms or lower halogenated hydrocarbons of 1 to 3 carbon atoms, with the halogens being selected from the group consisting of chlorine and fluorine, and the proportion of such pressurized gas in the product is from 3 to 90%.

11. A shaving cream product according to claim **10** wherein the organic sulfinate is triethanolamine toluene sulfinate.

12. A shaving cream product according to claim **10** wherein the organic sulfinate is potassium benzene sulfinate.

13. A shaving cream product according to claim 10 wherein the soap solution contains from 2 to 20% of a humectant selected from the group consisting of glycerine and sorbitol, 1 to 20% of alkyl phenyl polyoxyethylene ethanol, wherein the alkyl group is of 6 to 10 carbon atoms and the ethoxy content is from 1 to 50 ethoxies per mole, the product pH is from 7 to 10.5, the catalyst is present in sufficient quantity to accelerate the exothermic reaction so that the temperature of the dispensed shaving cream is raised to at least 120° F. in 30 seconds, and the propellant is a mixture of 85 to 90 parts of isobutane and 10 to 15 parts of propane.

14. A shaving cream product according to claim 13 wherein there are present about 20 parts of triethanolamine toluene sulfinate, 2.8 parts of hydrogen peroxide, 12 parts of mixed triethanolamine and sodium soaps of stearic acid, 5 parts sorbitol, 4 parts of nonyl phenyl polyoxyethylene ethanol, ¼ part of ammonium molybdate, 5 parts isobutane and 1 part propane, together with about 58 parts water.

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