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ALUMINUM SULFAMATE ANTIPERSPIRANT

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This invention relates to cosmetic astringent compositions and more particularly to improvements in anti-perspirant preparations.

Among the many anti-perspirants described as having the property of retarding or inhibiting the flow of perspiration the most effective have been found heretofore to be those containing aluminum salts of strong inorganic acids, e. g. hydrochloric, sulfuric, etc. Cosmetic preparations containing salts of these strong acids, however, have the very serious disadvantage of corroding or tendering clothing fabric, e. g., portions of garments which come in contact with areas of the body on which the preparation is applied. This corrosive action is especially noticeable on fabrics containing cellulosic materials such as cotton, rayon and the like. The corrosive effect that is detrimental to fabrics manifests itself particularly where the clothing portion carrying some of the anti-perspirant material is ironed or otherwise subjected to a relatively high temperature before removal of the anti-perspirant preparation. Even long continued contact at ordinary temperatures of cosmetic preparations containing aluminum salts of these mineral acids cause weakening or deterioration of the clothing fabric.

Of the many salts which have been used or described as useful anti-perspirants, aluminum chloride and aluminum sulfate are by far the most commonly used and have heretofore been considered to be the most effective. However, both salts show high corrosive action on cotton fabrics. This corrosive action is so severe that considerable research and investigation has been directed to a satisfactory reduction of the corrosive action without simultaneously reducing the anti-perspirant effectiveness of the salts. Because of its less corrosive action, aluminum sulfate is generally preferred over aluminum chloride.

It has now been discovered that the aluminum salt of sulfamic acid is a very efficacious perspiration retardant, having been found by tests to be definitely superior to the aluminum salt of sulfuric acid in this respect; and, of more importance, it has been observed that aluminum sulfamate is practically non-tendering to clothing fabrics. Under certain severe conditions, however, aluminum sulfamate may cause some discoloration of cellulosic fibers. The discoloration appears as a yellowish to light brown cast when an aluminum sulfamate-containing preparation is applied to and dried by heat on white fabrics made of cotton, linen or regenerated

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cellulosic fibers. Therefore, in order to use aluminum sulfamate in cosmetic preparations, it became necessary to eliminate or reduce to a satisfactory degree its property of causing discoloration of fabrics.

Extensive research was carried out with the object of finding a way to overcome this undesirable discoloration effect without impairing the efficiency of the aluminum sulfamate as an anti-perspirant. It was discovered that the discoloration tendency could be prevented or satisfactorily lessened by incorporating in the anti-perspirant preparation certain organic compounds in sufficient concentration. Compounds found to aid in preventing this discoloration, for convenience, may be classified into four general groups, as follows:

GROUP I

Amides which are neutral and contain the functional group

$$-\overset{\overset{O}{\|}}{C}-NH_2$$

and are soluble in aqueous aluminum sulfamate and which do not precipitate therefrom a compound containing aluminum, for example: urea, ethyl carbamate, formamide, and acetamide. The word "neutral" is used herein to mean that the compounds are practically unionized in aqueous solution.

GROUP II

Amino carboxylic acids which contain the functional group $\equiv C—NH_2$ and are soluble in aqueous aluminum sulfamate and which do not precipitate therefrom a compound containing aluminum, for example: glycine, α-alanine and β-alanine.

GROUP III

Compounds which are salts of non-hydroxy saturated carboxylic acids and ammonia bases, and which compounds are soluble in aqueous aluminum sulfamate and do not precipitate therefrom a compound containing aluminum. The ammonia base may be the unsubstituted ammonia, or hydrogen may be replaced by one or more alkyl radicals and this base when reacted with said carboxylic acid yields compounds such as, for example: diammonium malonate, ammonium acetate, diammonium oxalate, monoethanolamine acetate and thiethanolamine acetate.

GROUP IV

Compounds which contain the functional group $\equiv C—S—H$ and are soluble in aqueous aluminum

sulfamate and which do not precipitate therefrom a compound containing aluminum, for example: sodium mercaptopropanesulfonate (1,2), sodium 2-mercaptoethane-1-sulfonate, ammonium 2-mercaptoethane-1-sulfonate, ammonium thioglycolate, thioglycolic acid, thiourea and ethylene thiourea.

The extent of solubility of the substance used as a discoloration inhibitor in the aqueous sulfamate solution may vary with the various compounds and it is essential only that a sufficient quantity of the substance used go into solution to suitably inhibit the discoloration. In some cases the substance may be present in the composition in amounts greater than the limit of solubility without disadvantage. Further, the inhibiting substance used should not reduce the anti-perspirant property of the aluminum sulfamate, nor should it cause the finished preparation to have an objectionable odor, color or other undesirable characteristics such as cause irritation.

It is, of course, recognized that a few of the compounds listed above and many others which are inoperative in the present invention have been proposed for use in anti-perspirant preparations containing aluminum chloride or aluminum sulfate to prevent serious weakening or the destruction of fabric due to the corrosive action of these salts. In such preparations, however, the problem was solely to prevent tendering of the fabric since aluminum chloride and sulfate cause no discoloration and there was no reason to suggest that any known anti-tendering agent would be useful in preparations employing aluminum sulfamate for the entirely different function of preventing discoloration, particularly since tests had demonstrated that no anti-tendering agent was necessary in aluminum sulfamate preparations, nor was there anything to guide the search for anti-discoloring agents.

Test data have further indicated that aluminum sulfamate, either with or without the addition of a discoloration inhibitor from the above described groups produces definitely superior results in inhibiting perspiration when compared with like preparations which contain aluminum sulfate.

To secure such data, specific areas of skin of a number of human subjects were treated daily over a definite period and the perspiration inhibiting effects for aluminum sulfate and aluminum sulfamate were evaluated. The perspiration from two equal, comparable areas of skin with and without anti-perspirant treatment was periodically collected and weighed. For each measurement a per cent of perspiration-lessening effect was calculated as follows: Where X= weight of perspiration on untreated area and Y=weight of perspiration on like area treated with anti-perspirant material, then, the perspiration-lessening effect, as represented by (Z), expressed in per cent, is as follows:

$$Z=\frac{X-Y}{X}\times 100$$

The results obtained from the tests showed that aluminum sulfamate was from three to six or more times as effective as aluminum sulfate when comparable concentrations were used. In addition aluminum sulfamate has the advantage, as heretofore pointed out, that it has a much lower tendering-action on fabric, and such that anti-perspirant preparations containing aluminum sulfamate as the astringent may be used without the addition of corrosion-inhibiting

agents. Furthermore, where the cosmetic or other prepartion does not come in contact with cotton, muslin, rayon or the like substance whose chief ingredient is cellulose, the discoloration inhibitor may be omitted. For example, wool fibers do not give any discoloration when treated with solutions containing aluminum sulfamate. Where, however, the aluminum sulfamate-containing preparation is to be used for general purposes during which some discoloration may occur which would be objectionable, it is necessary to incorporate a suitable amount of an inhibitor such as described hereinbefore.

The proportion of inhibitor required to prevent discoloration varies with the particular inhibitor. In general, it has been found that when employing Group I, Group II and Group III compounds at least an equal molar proportion of the discoloration inhibitor to that of aluminum sulfamate should be used, and preferably about two to three mols of those inhibitors for each mol of aluminum sulfamate in solution is employed. With Group IV compounds about ¼ mol per mol of aluminum sulfamate is sufficient. Greater or less quantities of the discoloration inhibitor, or mixtures of different inhibitor compounds may of course be used so long as enough is incorporated to prevent discoloration where the same is objectionable.

In accordance with the present invention, novel anti-perspirant compositions containing aluminum sulfamate may be prepared and marketed in any desired form, e. g., as emulsions, suspensions, solutions, salves, creams, lotions and the like. Such preparations may comprise the usual ingredients including pigments, fillers, perfumes, etc., and they may be compounded in any suitable manner.

The proportion of aluminum sulfamate anti-perspirant ingredient to the total composition may be rather widely varied and depends to some extent upon the particular type of preparation, frequency of use, and other variable factors. In general, a composition should contain sufficient aluminum sulfamate to be effective when the usual amount of the preparation is applied to the skin and no more should be present than can be held in solution in the aqueous phase. Satisfactory results may be obtained in compositions in which the proportionate quantity of aluminum sulfamate incorporated ranges between about 5% and 50% by weight of the anti-perspirant preparation, and a preferred range lies between about 10% to 30% by weight.

Aluminum sulfamate may be incorporated into cream bases of widely varying composition either with or without a discoloration inhibitor. Generally speaking, such a cream includes an oily phase held in dispersion in an aqueous phase containing the anti-perspirant by one or more suitable emulsifying agents. The oily phase may include such materials as natural and synthetic oils, fats and waxes, e. g. spermaceti, palmityl palmitate, polymerized ethylene oxide ("Carbowax"), paraffin, sterols, mineral oils, vegetable oils and other esters of fatty acids, etc. Glycerine, propylene glycol, sorbitol and the like emollients may also be present.

Any suitable emulsifying agent may be employed which is sufficiently stable in acid media. Examples of emulsifying agents which have been found useful in preparing creams are: partial esters of fatty acids with glycerine, glycol or other polyhydric alcohol, preferably in combination with a stabilizer such as sodium monosulfate

monoglyceride of coconut oil fatty acids, diethyloleylamid phosphate, sodium lauryl sulfate, sodium alkyl aromatic sulfonate, etc.

As specific examples of preparations embodying the principles of this invention the following are given without intending to be limited thereby. The parts indicated are by weight.

Example 1

	Parts
Acid stabilized glyceryl monostearate [1]	16.0
Spermaceti wax	5.0
Sodium lauryl sulfate	1.5
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Urea	5.0
Water	54.0

[1] "Acid stabilized glyceryl monostearate" comprises glyceryl monostearate and a small amount (2 to 5% by wt.) of diethyloleylamid phosphate.

Example 2

	Parts
Diethylene glycol monostearate	16.0
Palmityl palmitate	3.0
Glycerine	1.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	2.5
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Thiourea	6.5
Water	52.5

Example 3

	Parts
Acid stabilized glyceryl monostearate	15.0
Glycerine	3.0
Spermaceti wax	5.0
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Formamide	7.7
Water	50.8

Example 4

	Parts
Acid stabilized glyceryl monostearate	15.0
Glycerine	3.0
Spermaceti wax	4.0
Sodium lauryl sulfate	1.0
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Acetamide	10.1
Water	48.4

Example 5

	Parts
Glyceryl palmitate	15.0
Palmityl palmitate	3.0
Glycerine	2.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	3.0
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Glycine	12.8
Water	45.7

Example 6

	Parts
Glyceryl monostearate	16.0
Spermaceti wax	3.0
Glycerine	3.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	3.0
Titanium dioxide	1.0
Aluminum sulfamate	18.0
Diammonium malonate	11.9
Water	44.1

Example 7

	Parts
Glyceryl monostearate	15.0
Spermaceti wax	4.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	3.0
Titanium dioxide	0.5
Aluminum sulfamate	18.0
Ammonium acetate	13.2
Water	46.3

Example 8

	Parts
Acid stabilized glyceryl monostearate	15.0
Spermaceti wax	5.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	3.0
Glycerine	2.0
Titanium dioxide	0.5
Aluminum sulfamate	13.0
Triethanolamine acetate	12.9
Water	48.6

Example 9

	Parts
Glyceryl monostearate	13.00
Spermaceti wax	3.00
Stearyl alcohol	3.00
Mineral oil	1.00
"Igepon T" (sodium β-oleylethane-amid-sulfonate)	2.50
Titanium dioxide	0.50
Aluminum sulfamate	13.00
Ammonium 2-mercaptoethane-1-sulfonate	1.64
Water	63.36

Example 10

	Parts
Glyceryl monostearate	15.00
Spermaceti wax	3.00
Mineral oil	2.00
Glycerine	2.00
Titanium dioxide	0.40
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	3.00
Aluminum sulfamate	18.00
Sodium mercaptopropanesulfonate (1,2)	2.54
Water	54.06

Example 11

	Parts
Acid stabilized glyceryl monostearate	13.00
Spermaceti wax	3.00
Stearyl alcohol	2.00
"Igepon T" (sodium β-oleylethane-amid-sulfonate)	3.00
Glycerine	2.50
Aluminum sulfamate	22.50
Ammonium thioglycolate	2.34
Water	51.66

Example 12

	Parts
Acid stabilized glyceryl monostearate	10.00
Glyceryl monostearate	4.00
Spermaceti wax	4.00
Mineral oil	2.00
"Igepon T" (sodium β-oleylethane-amid-sulfonate)	2.50
Titanium dioxide	0.50
Aluminum sulfamate	18.00
Thioglycolic acid	1.59
Water	57.41

Example 13

	Parts
Glyceryl monostearate	13.0
Spermaceti wax	4.0
Glycerine	1.0
Sodium salt of sulfated monoglyceride of coconut oil fatty acids	2.3
Titanium dioxide	0.3
Aluminum sulfamate	20.0
Ethylene thiourea	1.6
Water	57.8

The aluminum sulfamate cream preparations of Examples 1 through 13 were tested to determine the effectiveness of the various inhibitors in lessening the discoloration tendency on fabrics. In carrying out the tests the cream was smeared over a cotton swatch (2" x 4" strip) until all of the fabric was covered evenly with no excess cream on the surface. On the reverse side of the strip three drops of water were added to moisten the cloth, and thereafter the strip was placed in an oven and baked at about 214° F. for thirty minutes. These swatches were tested alongside a cotton swatch smeared with a like aluminum sulfamate cream preparation which contained no discoloration inhibitor. Even under the severe conditions of this test, the strip treated with the uninhibited cream was discolored to a greater extent than any of the strips treated with creams of Examples 1 to 13, and in the case of Examples 1, 2, 3, 5, 6, 7, 9, 10 and 12, there was practically no discoloration. Further, it has been ascertained from tests of the cream containing the inhibitor giving the least effect under the severe conditions of the above test that even this substance was effective in inhibiting this undesirable coloring effect on fabric when tested under conditions comparable to those encountered during the normal use of the anti-perspirant.

Examples of suitable aluminum sulfamate anti-perspirant solutions which may be used in liquid form or as the water phase in a cream or emulsion-type preparation, such as described in Examples 1 to 13, are as follows, the parts being by weight:

Example A

	Parts
Aluminum sulfamate	24.9
Urea	14.2
Water	60.9

Example B

	Parts
Aluminum sulfamate	24.9
Ethyl carbamate (urethane)	14.1
Water	61.0

Example C

	Parts
Aluminum sulfamate	24.9
Thiourea	6.0
Water	69.1

Example D

	Parts
Aluminum sulfamate	25.0
Glycine	17.8
Water	57.2

Example E

	Parts
Aluminum sulfamate	25.0
β-alanine	21.2
Water	53.8

Example F

	Parts
Aluminum sulfamate	25.0
Diammonium oxalate	17.0
Water	58.0

Example G

	Parts
Aluminum sulfamate	25.0
Monoethanolamine acetate	25.0
Water	50.0

Example H

	Parts
Aluminum sulfamate	24.9
Sodium 2-mercaptoethane-1-sulfonate	3.1
Water	72.0

Example I

	Parts
Aluminum sulfamate	25.0
Sodium mercaptopropanesulfonate (1,2)	3.4
Water	71.6

Example J

	Parts
Aluminum sulfamate	25.0
α-Alanine	21.2
Water	53.8

The effectiveness of the various discoloration inhibitors in Examples A to J inclusive was tested by dipping a cotton swatch into each solution and hetaing in an oven at about 214° F. for thirty minutes. In each case the discoloration of a similarly treated swatch which has been dipped into a solution of aluminum sulfamate containing no inhibitor was much greater than any of the swatches dipped in the solutions of Examples A through J.

Aqueous solutions of aluminum sulfamate suitable for use in compounding the anti-perspirant compositions of the invention may be prepared by any appropriate method, such as by reaction of a theoretical amount of sulfamic acid with aluminum hydroxide gel to give a clear solution of aluminum sulfamate. Another method which may be used comprises the reaction of barium sulfamate in an aqueous medium with a theoretical amount of aluminum sulfate to form insoluble barium sulfate which may be removed to leave a clear solution of aluminum sulfamate.

Although the invention has been described in detail and exemplified by numerous examples, it will be understood that the principles of the invention may be made use of by utilizing aluminum sulfamate with modified formulae such as will occur to those skilled in the art.

What is claimed is:

1. A perspirant inhibiting or retarding preparation comprising an aluminum salt of sulfamic acid in an effective amount from about 5 to about 50% by weight, said aluminum salt having a tendency to discolor cellulosic fibers, and in an amount sufficient to inhibit said discoloration an organic nitrogen compound selected from the class consisting of (*a*) amides which are neutral and contain the functional group

$$-\overset{\overset{O}{\|}}{C}-NH_2$$

(*b*) amino carboxylic acids which contain the functional group $\equiv C-NH_2$, and (*c*) compounds which are salts of non-hydroxy non-mercapto saturated carboxylic acids and ammonia bases, said compound being soluble in aqueous aluminum sulfamate and not precipitating therefrom a compound containing aluminum.

2. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and a neutral amide containing the function group

$$-\overset{\overset{O}{\|}}{C}-NH_2$$

which is soluble in aqueous aluminum sulfamate and which does not precipitate therefrom a compound containing aluminum, the amount of said amide being at least in about equal molar proportion to that of said aluminum sulfamate and sufficient to inhibit said discoloration.

3. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and an ammonium salt of a non-hydroxy non-mercapto saturated carboxylic acid and which is soluble in aqueous aluminum sulfamate and does not precipitate therefrom a compound containing aluminum, the amount of said ammonium salt being at least in about equal molar proportion to that of said aluminum sulfamate and sufficient to inhibit said discoloration.

4. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and an amino carboxylic acid compound containing the functional group $\equiv C-NH_2$ and which compound is soluble in aqueous aluminum sulfamate and does not precipitate therefrom a compound containing aluminum, the amount of said amino carboxylic acid compound being at least in about equal molar proportion to that of said aluminum sulfamate and sufficient to inhibit said discoloration.

5. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and urea in an amount sufficient to inhibit said discoloration.

6. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and diammonium malonate in an amount sufficient to inhibit said discoloration.

7. A perspirant inhibiting or retarding preparation comprising a water-containing vehicle, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and, and glycine in an amount sufficient to inhibit said discoloration.

8. A perspirant inhibiting or retarding preparation in the form of a cream comprising fatty material emulsified with a water-containing phase, aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and urea in an amount sufficient to inhibit said discoloration.

9. A cosmetic preparation for inhibiting or retarding perspiration comprising an oily phase held in dispersion in an aqueous phase, said aqueous phase containing aluminum sulfamate in an effective amount from about 5 to about 50% by weight, said aluminum sulfamate having a tendency to discolor cellulosic fibers, and in an amount sufficient to inhibit said discoloration an organic nitrogen compound selected from the class consisting of (*a*) amides which are neutral and contain the functional group

$$-\overset{\overset{O}{\|}}{C}-NH_2$$

(*b*) amino carboxylic acids which contain the functional group $\equiv C-NH_2$, and (*c*) compounds which are salts of non-hydroxy non-mercapto saturated carboxylic acids and ammonia bases, said compound being soluble in aqueous aluminum sulfamate and not precipitating therefrom a compound containing aluminum.

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