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3,256,155

DENTIFRICE COMPOSITION

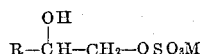
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No Drawing. Filed Apr. 11, 1962, Ser. No. 186,630

9 Claims. (Cl. 167-93)

This invention relates to 2-hydroxyalkyl sulfates, alkali metal salts thereof, and to their method of preparation. The invention additionally relates to detergent and dentifrice formulations containing 2-hydroxyalkyl sulfates and their alkali metal salts as active ingredients.

The compounds of the formula



wherein R is an alkyl group having from 8 to 18 carbon atoms, and M is selected from the group consisting of hydrogen and alkali metals have been discovered.

The novel compounds of this invention are excellent surface active agents and are useful in detergent formulations. Certain of the 2-hydroxyalkyl sulfates show excellent detergency without conventional inorganic builder salts, and show a moderate response to the conventional inorganic builder salts such as alkali metal sulfates, carbonates, silicates, phosphates, borates and mixtures thereof. Additionally, they show moderate activity as lime soap scum dispersants. Accordingly, the 2-hydroxyalkyl sulfates are useful in dishwashing detergents, non-soap bars, soap bars, bars containing mixtures of soaps and non-soaps, and to other applications known to those skilled in the art where surface active properties are desired.

A particularly useful and unexpected property of 2-hydroxyalkyl sulfates is realized in their use as dentifrice detergents. Most dentifrice formulations now commercially marketed contain surface active agents in low concentrations. The principal function of the surfactant is to provide an adequate foam level. Beyond providing foam, it is obvious that a desirable surfactant should not interfere with the flavor of the dentifrice formulation. Many of the commonly used dentifrice detergents, including sodium lauryl sulfate, have the disadvantage of giving an "orange juice effect," an unpleasant flavor effect caused by interaction of citrus juice and the detergent. The effect is noted by many people when they ingest orange juice shortly after brushing their teeth. One means of avoiding this flavor effect is by the use of a toothpaste containing a combination of sodium lauryl sulfate and a monoglyceride sulfonate of a fatty acid, as described in U.S. Patent No. 2,812,284.

It has now been discovered that the same combination of desirable properties, namely, good foam level and the absence of an unpleasant flavor effect by interaction with citrus juice, is provided by using the 2-hydroxyalkyl sulfates of this invention in dentifrices as the active detergent.

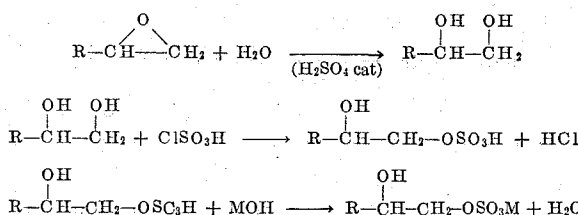
In addition to the detergent, the dentifrices of this invention include an abrasive and other conventional ingredients such as binders, sweeteners, flavor, preservative, and humectant.

The compounds of this invention are prepared by hydrolyzing a long chain 1,2-epoxy compound to produce the corresponding 1,2-diol, and subsequently sulfating the 1,2-diol to produce the corresponding 2-hydroxyalkyl-sulfuric acid, which is then neutralized with an alkali metal hydroxide.

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The hydrolysis of the epoxy compound is carried out in a suitable solvent in the presence of 10% aqueous sulfuric acid as a catalyzing agent. Sulfation is preferably accomplished with chlorosulfonic acid by adding the chlorosulfonic acid dropwise while stirring a solution of the reaction mixture. The solvent used may be any solvent which is inert to attack by chlorosulfonic acid. Chlorinated solvents such as chloroform are especially advantageous. The chlorosulfonic acid and 1,2-diol should be mixed in approximately equimolar quantities. The synthesis of the compounds of this invention is summarized by the following equations:

The hydrolysis of the epoxy compound is carried out in a suitable solvent in the presence of 10% aqueous sulfuric acid as a catalyzing agent. Sulfation is preferably accomplished with chlorosulfonic acid by adding the chlorosulfonic acid dropwise while stirring a solution of the reaction mixture. The solvent used may be any solvent which is inert to attack by chlorosulfonic acid. Chlorinated solvents such as chloroform are especially advantageous. The chlorosulfonic acid and 1,2-diol should be mixed in approximately equimolar quantities. The synthesis of the compounds of this invention is summarized by the following equations:



The 1,2-epoxide starting materials may be prepared by conventional methods such as oxidation of olefin compounds derived from petroleum sources. Likewise, the 1,2-diol may be prepared according to other conventional methods such as hydrolysis of chlorohydrins and the like.

It is apparent from the above discussion that an important step in the preparation of the compounds of this invention is the sulfation of the 1,2-diol. The use of chlorosulfonic acid as the sulfating agent produces the desired 2-hydroxyalkyl sulfate preferentially to the unwanted 1-hydroxyalkyl sulfate.

Other customary sulfating agents may be used in place of the chlorosulfonic acid with similar results. Representative sulfating agents which are suitable include concentrated sulfuric acid, sulfur trioxide alone or in combination with air or a stabilizer, and the like.

The following examples describe the preparation and characteristics of the compounds of this invention, and also describe their usefulness as active ingredients in detergent and dentifrice formulations.

EXAMPLE I

Preparation of sodium 2-hydroxytetradecyl sulfate

Tetradecane-1,2-diol was first prepared according to the following procedure:

A mixture of 42.4 g. (0.2 M) of 1,2-epoxytetradecane, 225 ml. of 1,4-dioxane and 40 ml. of 10% aqueous sulfuric acid was stirred and heated to 50° C. A homogeneous solution was obtained at this temperature and the reaction was allowed to proceed for four and one-half hours. The resultant solution was poured into 1500 ml. of ice water. A white precipitate was obtained and separated by filtration. The wet residue was dissolved in 1500 ml. of boiling petroleum ether and the petroleum ether solution was decanted from the aqueous layer. On cooling, the product, tetradecane-1,2-diol, precipitated out of the petroleum ether. After filtration and drying, the product weighed 30 g. and melted at 68.2-68.8° C. This corresponded to a 65% yield.

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Sodium 2-hydroxytetradecyl sulfate was then prepared by dissolving 11.5 g. of the tetradecane-1,2-diol (0.05 mole) in a minimum amount of chloroform, and placing the solution in a 250 ml. 3-necked flask equipped with a mechanical stirrer and a dropping funnel. 5.9 g. of chlorosulfonic acid (0.05 mole) was added dropwise with stirring. Stirring was continued for 10 minutes after the addition was complete. The acidic reaction mixture was poured with stirring into sufficient 20% sodium hydroxide solution to bring the pH of the resulting mixture to 10-11. After evaporation of the chloroform and water, the crude product was recrystallized from ethanol, yielding 11.9 g. of 98% pure 2-hydroxytetradecyl sulfate (72% of theory). Analysis of the product gave 9.43% S, while the calculated amount of S was 9.65%.

EXAMPLE II

Tetradecane-1,2-diol was prepared as in Example I, except that tetrahydrofuran was used as a solvent in place of the 1,4-dioxane, the reaction mixture was refluxed and the reaction time was extended to six hours. Comparable yields of tetradecane-1,2-diol were obtained.

Tetradecane-1,2-diol was also prepared using acetone to replace tetrahydrofuran as the solvent, the remaining experimental details being the same as above. Comparable yields of tetradecane-1,2-diol were obtained.

EXAMPLE III

Sodium 2-hydroxydecyl sulfate was prepared as follows: 6.6 g. of decane-1,2-diol (0.038 mole) was dissolved in chloroform and 4.9 g. of chlorosulfonic acid (0.041 mole) was added dropwise with stirring. After adding the chlorosulfonic acid, stirring was continued for an additional 1½ hours. The acidic reaction mixture was poured with stirring into sufficient 20% sodium hydroxide solution to bring the pH of the resulting mixture to 10-11. After evaporation of the water and chloroform, the crude product was recrystallized from ethanol, yielding 6.1 g. of sodium 2-hydroxydecyl sulfate. The yield was 67% of the theoretical.

EXAMPLE IV

Sodium 2-hydroxyoctadecyl sulfate was prepared as follows:

30.0 g. of octadecane-1,2-diol (0.105 mole) was dissolved in 300 ml. of chloroform and 12.8 g. of chlorosulfonic acid (0.11 mole) was added to the solution dropwise with stirring. The stirring was continued for two hours after addition was complete. The acidic reaction mixture was poured with stirring into sufficient 15% sodium hydroxide solution to bring the pH of the mixture to 10-11. After evaporation of the water and chloroform the crude product was recrystallized from ethanol, yielding 32.1 g. of sodium 2-hydroxyoctadecyl sulfate. The yield was 78.7% of the theoretical.

EXAMPLE V

A sodium 2-hydroxyalkyl sulfate, wherein the alkyl portion was a mixture having carbon chain lengths ranging from C₁₁ to C₁₅ was prepared as follows:

50.0 g. of an alkane-1,2-diol, wherein the alkane portion was a mixture having carbon chain lengths ranging from C₁₁ to C₁₅ (0.26 mole) was dissolved in 255 ml. of chloroform. 33.8 g. of chlorosulfonic acid (0.28 mole) was added to the solution dropwise with stirring. Stirring was continued for 2 hours after addition was complete. The acidic reaction mixture was poured with stirring into sufficient 12% sodium hydroxide solution to bring the pH of the resulting mixture to 10-11. After evaporation of the water and chloroform, the crude product was dissolved in hot ethanol, the undissolved sodium chloride filtered off, and the pure product recovered from the filtrate. The yield was 45.8 g.

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EXAMPLE VI

A series of the compounds of this invention was prepared by the method described in Example I. The detergency characteristics of these compounds were evaluated with a Terg-O-Tometer detergency test. Corresponding alkyl sulfates were evaluated by the same test, for purposes of comparison.

The Terg-O-Tometer test gives an empirical measurement of the amount of soil removed from the fabric under simulated washing conditions. Sample swatches of cloth soiled in a standard manner with a standard soil, are placed in a miniature washing machine, the Terg-O-Tometer apparatus, and are laundered in the presence of a measured amount of detergent and water of a standard hardness. A Terg-O-Tometer apparatus is described in the Journal of the American Oil Chemists' Society, volume 27, May 1950, pages 153-159. After rinsing and drying, the reflectance of the cloths is measured and compared with the reflectance of the soiled cloths before washing. In the detergency tests referred to herein, the Terg-O-Tometer apparatus was maintained in a water bath adjusted to maintain the temperature of the washing solution at 120° F. ±2° F. The paddle oscillation was brought to 90 complete cycles per minute and the paddle oscillated through a 320° arc.

With the agitators in position on the machines, the detergent was added in the desired amount to the washpot of the machine. 1250 ml. of water having a hardness of 180 parts per million CaCO₃ (60 parts magnesium and 120 parts calcium calculated as calcium carbonate), were added. The machine was started and the solution agitated until the detergent was dissolved. Four pieces of soiled cloth approximately 4½ inches by 6 inches were added and the washing was continued for twenty minutes, after which the test swatches were removed from the solution and hand squeezed. The washpot was refilled with clear rinse water of the same hardness used for washing at a temperature of 120° F. ±2° F. and, with the agitators running, the cloths were rinsed for five minutes. The cloths were then removed, hand squeezed, and ironed dry. The reflectance of the cleaned cloths was measured with a Hunter reflectometer using the green filter.

The Terg-O-Tometer test was carried out in duplicate. The reflectance values in the table below represents the average of the actual reflectance reading taken from 8 cloth swatches. Each of the 2-hydroxyalkyl sulfates and the alkyl sulfates was evaluated alone and in the presence of tetrapotassium pyrophosphate, a conventional builder. Table I summarizes the results obtained.

TABLE I.—COMPARISON OF DETERGENCY OF SODIUM ALKYL SULFATES AND SODIUM 2-HYDROXYALKYL SULFATES

Compound	Reflectance Readings, Hunter Reflectometer with Green Filter	
	Level, 0.05% by weight	0.025% by weight of compound plus 0.05% by weight of TKPP ¹
Sodium dodecyl sulfate.....	42.9	43.8
Sodium tetradecyl sulfate.....	40.2	48.4
Sodium hexadecyl sulfate.....	41.8	47.8
Sodium octadecyl sulfate.....	40.7	42.3
Sodium 2-hydroxydodecyl sulfate.....	41.7	43.7
Sodium 2-hydroxytetradecyl sulfate.....	43.8	43.2
Sodium 2-hydroxyhexadecyl sulfate.....	47.0	49.5
Sodium 2-hydroxyoctadecyl sulfate.....	46.1	46.2
Sodium 2-hydroxyalkyl (C ₁₁ -C ₁₅) sulfate.....	41.3	45.0
Dodecylbenzenesulfonate; sodium salt.....	40.7	46.2
TKPP ¹	42.0	
Water.....	40.2	
Soil Cloth-Initial Average.....	39.7	

¹ Tetrapotassium pyrophosphate.

The data of Table I shows that 2-hydroxyalkyl sulfates are superior to the corresponding alkyl sulfates, particularly in the absence of a phosphate builder. Maximum detergency in the 2-hydroxyalkyl sulfate series is obtained at higher alkyl carbon chain lengths than in the alkyl sulfate series. Since compounds of longer carbon chain lengths are, in general, milder towards the skin than shorter chain compounds, a distinct advantage in this regard resides with the 2-hydroxyalkyl sulfates.

EXAMPLE VII

A series of 2-hydroxyalkyl sulfates was prepared and tested for mildness or lack of irritation potential toward the skin by means of the Repeat Animal Patch test. This test measures the primary irritation potential, that is, the inverse of mildness, of toilet bars and detergents.

The test is conducted by applying patches saturated with the test solution to young, adult Swiss albino mice, usually four for each test. The mice are patched with the test solutions for 75 minutes each day for four successive days. Six applications with friction are made during the 75-minute period. The treated area is maintained moist during the patch period by covering with a rubber dam.

EXAMPLE VIII

To many individuals, citrus juice has an undesirable bitter taste when ingested shortly after their teeth have been cleaned with a dentifrice containing sodium lauryl sulfate or one of the many other widely used dentifrice detergents. This effect is well known. U.S. Patent No. 2,812,284 describes a combination of sodium lauryl sulfate and a monoglyceride sulfonate of a fatty acid which provides an acceptable foam and which, at the same time, does not evidence the "orange juice flavor effect."

A panel of 8 to 9 subjects sensitive to this effect was asked to use unmarked samples of various dentifrices, some containing sodium lauryl sulfate and some containing one of a series of 2-hydroxyalkyl sulfates. In the test, the subjects brushed their teeth, waited for five minutes and then ingested orange juice. Where no objectionable taste was found in the orange juice by the subject, the subject listed the dentifrice as being acceptable.

The formulae of the various dentifrices investigated are given below. Each dentifrice contained an abrasive and other conventional dentifrice ingredients in addition to the detergent being tested:

Ingredient	Toothpaste, percent				
	A	B	C	D	E
Dicalcium phosphate dihydrate	50.78	50.61	50.45	49.22	50.78
Other inorganic abrasives	5.42	5.41	5.39	5.19	5.42
Binder	0.51	0.50	0.50	0.49	0.51
Humectant	23.02	22.94	22.88	22.40	22.16
Sweetener	0.13	0.13	0.13	0.13	0.13
Water	18.90	18.82	18.77	18.66	18.90
Flavor	0.89	0.89	0.88	0.86	0.89
Detergent	0.30	0.65	0.95	3.00	1.16
Preservative	0.05	0.05	0.05	0.05	0.05
	100.00	100.00	100.00	100.00	100.00

After the fourth patch, the animals are sacrificed, the treated areas excised, and the tissues prepared for histological analysis (paraffin imbedding; slides stained with Eosin Methylene Blue).

The criterion of mildness is based on the degree of epidermal destruction incurred after repeated exposure to the test preparation at high concentrations. The exaggerated levels are necessary since the epidermis usually remains intact when treated with most detergents at use concentrations.

Mildness ratings based on the degree of epidermal erosion observed histopathologically are as follows:

- 0—No epidermal erosion (very mild)
- 1—Small areas of erosion (fair mildness)
- 2—25% to 50% epidermal erosion (moderately irritating)
- 3—Over 50% epidermal erosion (strongly irritating)

The 2-hydroxyalkyl sulfates were tested by this procedure, together with a corresponding series of sodium alkyl sulfates, both as 2% aqueous solutions. Results of this test are listed in Table II.

TABLE II

Compound:	Mildness rating
Sodium decyl sulfate	1
Sodium dodecyl sulfate	3
Sodium tetradecyl sulfate	0
Sodium hexadecyl sulfate	0
Sodium 2-hydroxydecyl sulfate	0
Sodium 2-hydroxydodecyl sulfate	1 0-1
Sodium 2-hydroxytetradecyl sulfate	1 0-1
Sodium 2-hydroxyhexadecyl sulfate	1

¹ Differences between 0 and 0-1 are not considered significant in this test.

Toothpaste Formula F

Ingredient:	Percent
Dicalcium phosphate dihydrate	49.33
Alumina	0.25
Binder	0.95
Humectant	22.25
Sweetener	0.12
Water	24.89
Flavor	0.88
Detergent	1.25
Preservative	0.08
	100.00

Tooth powder Formula G

Ingredient:	Percent
Insoluble sodium metaphosphate	72.54
Dicalcium phosphate dihydrate	19.13
Magnesium silicate	4.01
Binder	0.50
Sweetener	0.20
Wetting agent	1.00
Flavor	1.67
Detergent	0.95
	100.00

The foaming ability of the dentifrice described above was also evaluated in terms of foam quality and foam volume. The foam volume was measured by transferring a two-gram sample of the dentifrice into a 50 ml. beaker containing 5 ml. of distilled water. The mixture was stirred gently until thoroughly dispersed and then transferred to a 100 ml. graduated cylinder. The beaker was washed with 15 ml. of water and the washings added to

the cylinder. The cylinder was then turned 25 times and permitted to rest for five minutes, after which the foam volume was read.

The results of the orange juice flavor effect evaluation and the foam evaluation are given in Table III below.

TABLE III

Dentifrice Base	Detergent, Type	Level, percent by weight	Orange Juice Effect, Number of panelists		Foam	
			Acceptable	Unacceptable	Quality	Volume, ml.
A-----	Sodium 2-hydroxytetradecyl sulfate-----	0.30	6	2	Poor-----	21
B-----	Sodium 2-hydroxydodecyl sulfate-----	0.65	9	0	do-----	20
C-----	Sodium 2-hydroxydodecyl sulfate-----	0.65	6	3	Good-----	36
C-----	Sodium 2-hydroxytetradecyl sulfate-----	0.30				
C-----	Sodium 2-hydroxydodecyl sulfate-----	0.30	7	1	do-----	46
C-----	Sodium 2-hydroxytetradecyl sulfate-----	0.65				
D-----	Sodium 2-hydroxydodecyl sulfate-----	3.00	6	2	Poor-----	37
E-----	Sodium lauryl sulfate-----	1.16	0	8	Good-----	45
F-----	Sodium 2-hydroxyoctadecyl sulfate-----	1.25	9	0	Poor-----	8
G-----	Sodium 2-hydroxydodecyl sulfate-----	0.65	7	1	Good-----	38
G-----	Sodium 2-hydroxytetradecyl sulfate-----	0.30				

Additional tests by a 200 member test panel made to evaluate the flavor of the 2-hydroxyalkyl sulfates as toothpaste surfactants indicated that dentifrices containing the 2-hydroxyalkyl sulfates of this invention have an overall flavor which is generally acceptable.

EXAMPLE XI

An important property of toothpaste detergents is the ability to produce foam. The following test procedure was used to measure the foaming ability of toothpaste formulations containing the 2-hydroxyalkyl sulfate of this invention:

Two gram samples of an experimental toothpaste formulation similar to Toothpastes A-E described in Example VIII, containing 1% and 1.5% detergent were each introduced into a 50 ml. beaker containing 5 ml. of distilled water. The toothpaste was thoroughly dispersed by gentle stirring, and the dispersion was then transferred to a 100 ml. graduated cylinder. The beaker was washed with 15 ml. of distilled water and the washings also transferred to the cylinder. The cylinder was then inverted 25 times and allowed to rest for five minutes before reading the foam volume. The experimental results from a series of tests run in this manner are summarized in Table IV.

TABLE IV

Foaming agent:	Foam volume, ml.
1% sodium lauryl sulfate -----	43
1.5% sodium 2-hydroxydodecyl sulfate -----	36
1.5% sodium 2-hydroxytetradecyl sulfate -----	80
1.5% sodium 2-hydroxyhexadecyl sulfate -----	20

EXAMPLE X

Mixtures of the 2-hydroxyalkyl sulfates of this invention have been found useful as toothpaste detergents. For example, on comparison with a commercial toothpaste, a toothpaste containing 1.25% of 2-hydroxydodecyl sulfate was marginally less acceptable because it was considered slightly deficient in foam. Toothpastes containing 1.25% of sodium 2-hydroxytetradecyl sulfate developed more copious foam than products with the dodecyl analog, but gave a slightly bitter "orange juice effect." However, by using a mixture of 0.65% of the dodecyl analog and 0.3% of the tetradecyl analog, a toothpaste was obtained which was satisfactory with regard to both foaming ability, overall flavor and absence of the "orange juice effect," and the paste contained a total level of only 0.95% detergents.

EXAMPLE XI

A sodium 2-hydroxyalkyl sulfate, wherein the alkyl portion was a mixture having carbon chain lengths rang-

ing from C₁₅ to C₂₀ was prepared according to the method outlined in Example V. The detergency characteristics of this composition were compared with those of the mixed C₁₁-C₁₅ 2-hydroxyalkyl sulfate of Example V, using the Terg-O-Tometer test outlined in Example VI.

The following Table V gives the reflectance readings obtained after washing the soiled cloths in water of 180 p.p.m. hardness.

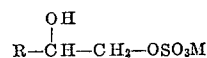
TABLE V

Compound	Reflectance Readings, Hunter Reflectometer with Green Filter	
	Level, 0.05% by weight	0.025% by weight of compound plus 0.05% by weight of TKPP ¹
40 Sodium 2-hydroxyalkyl (C ₁₁ -C ₁₅) sulfate-----	44.5	47.5
Sodium 2-hydroxyalkyl (C ₁₅ -C ₂₀) sulfate-----	51.1	54.2
Dodecylbenzenesulfonate, sodium salt-----	41.8	50.2
TKPP ¹ -----	44.0	-----
Water-----	41.2	-----
Soil Cloth-Initial Average-----	41.6	-----

¹ Tetrapotassium pyrophosphate.

We claim:

1. A dentifrice composition comprising an abrasive and a compound having the formula



wherein R is alkyl having from 8 to 18 carbon atoms and M is selected from the group consisting of hydrogen and the alkali metals.

2. The dentifrice composition of claim 1, wherein the compound is 2-hydroxydecyl sulfate.

3. The dentifrice composition of claim 1, wherein the compound is 2-hydroxydodecyl sulfate.

4. The dentifrice composition of claim 1, wherein the compound is 2-hydroxytetradecyl sulfate.

5. The dentifrice composition of claim 1, wherein the compound is sodium 2-hydroxydodecyl sulfate.

6. The dentifrice composition of claim 1, wherein the compound is sodium 2-hydroxytetradecyl sulfate.

7. A dentifrice composition comprising an abrasive and a mixture containing 2-hydroxydodecyl sulfate and 2-hydroxytetradecyl sulfate in a ratio between about 30:65 and 65:30.

8. A dentifrice composition comprising an abrasive and a mixture containing 2-hydroxydodecyl sulfate and 2-hydroxytetradecyl sulfate in a ratio of about 30:65.

9. A dentifrice composition comprising an abrasive and a mixture containing 2-hydroxydodecyl sulfate and 2-hydroxytetradecyl sulfate in a ratio of about 65:30.

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