1282458

PATENT SPECIFICATION (11) 1282458

NO DRAWINGS

(21) Application No. 37589/69 (22) Filed 25 July 1969
(31) Convention Application No. 53303 (32) Filed 26 July 1968 in
(33) Japan (JA)
(45) Complete Specification published 19 July 1972
(51) International Classification A61K 7/16
(52) Index at acceptance A5B 772

(54) DENTIFRICE COMPOSITION

(71) We, LION HAMIGAKI KABUSHIKI KAISHA, of 3-7, Honjo 1-chome, Sumida-ku, Tokyo-to, Japan, a corporation duly organized and existing under the laws of Japan, LION YUSHI KABUSHIKI KAISHA, of 2-26, Yokoami 1-chome, Sumida-ku, Tokyo-to, Japan, a corporation duly organized and existing under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to dentifrice compositions.

Usually, foaming agents, such as detergents, are added to give dentifrice compositions foaming properties; the surface active agents shown in the following Table 1 are generally used as foaming agents. They have their own merits and defects, respectively, as components of dentifrices and the preparation thereof. Some tend to greatly reduce the viscosity index of the dentifrice, to lower its commercial value, due to changes in colour and flavour of the composition which they may produce during storage, or to impair the quality of the composition itself. Furthermore, some tend to corrode the containers used for the dentifrice compositions, particularly the inside surface of metal tubes. However, it has been necessary to prepare dentifrices having some of these defects.

TABLE 1

Foaming agent		Foaming	Taste	Orange Juice effect	Stimulus to mucous membrane
Sodium acylsarcosinate	C_{12}	A	C	C	B
"	C_{14}	B	C	C	B
Sodium monoglyceride sulfate	C_{12}	B	C	B	D
"	C_{14}	D	C	A	C
Sodium fatty acid monoglyceride sulfonate	C_{12}	B	D	C	B
"	C_{14}	C	D	B	B
Sodium alkylsulph-acetate	C_{12}	B	D	C	B
"	C_{14}	B	C	C	B
Lauroyldimethylamine oxide		D	D	B	B
Lauroyldiethanolamide		D	C	B	B

In the table:— A = Excellent
B = Good
C = Fair
D = Poor

[*Price 25p*]

The Orange Juice effect is the property by which a dentifrice does not impair the taste of Orange Juice or Fruits when taken just after using the dentifrice.

It is an object of the present invention to reduce these defects of ordinary dentifrice compositions and to improve the cleaning action and refreshing effect in the mouth which can be obtained.

Another object of the present invention is to provide a dentifrice composition which is pleasant to use, due to good flavour and soft-touch in the mouth, by improving the foaming effect so as to obtain considerable and fine foamability.

The dentifrices of the invention are easy and economic to manufacture and possess a good Orange juice effect. They also show good cleansing and deodouring effects in the mouth, owing to improved dispersing and stabilizing properties.

The present invention further helps produce a dentifrice of excellent flavour which gives abundant foam and which does not irritate the mucous membrane of the mouth in the way that some known dentifrices do and which has an increased polishing effect.

The present invention provides a dentifrice composition comprising a water-soluble hydroxyalkanesulphonate such as a 3-hydroxyalkanesulphonate or 4-hydroxyalkanesulphonate or a mixture of two or more of these, which acts as foaming agent in a dentifrice base, which may comprise a humectant, binder, polishing agent, flavouring agent, medicating agent, sweetener and water, or at least some of these.

The hydroxyalkanesulphonates used in the present invention may be 3-hydroxyalkanesulphonates and/or 4-hydroxyalkanesulphonates which are represented by the general formulae

$$R—CH_2—CH(OH)—CH_2CH_2SO_3M \quad (1)$$

$$R—CH(OH)—CH_2—CH_2CH_2SO_3M \quad (2)$$

(wherein, R is an alkyl group with or without a branched chain having 8—20 carbon atoms in the chain and M is an alkali or alkaline earth metal, ammonium or alkanolamine). The blending ratio (when two or more of such compounds are used) may be optionally selected, the compounds and their proportions being selected in accordance with their effectiveness. Mixtures consisting of some hydroxyalkanesulphonates having different numbers of carbon atoms may be used, the total number of carbon atoms in each being preferably from 12 to 24.

The hydroxyalkanesulphonate may be present in an amount of 0.1 to 10% by weight of the dentifrice base.

The hydroxyalkanesulphonate used can be prepared in any suitable manner. For example 3-hydroxyalkanesulphonate is made by the following steps;

$$(1)\ RCOCl + CH_2=CH_2 \xrightarrow{\text{Friedel crafts catalyst}} RCO—CH_2—CH_2—Cl$$

$$(2)\ RCO—CH_2—CH_2—Cl + Na_2SO_3 \rightarrow RCO—CH_2CH_2—SO_3Na + NaCl$$

$$(3)\ 2RCO—CH_2—CH_2—SO_3Na + H_2 \rightarrow 2RC\,H(OH)—CH_2—CH_2SO_3Na$$

4-Hydroxyalkanesulphonate is made by the following steps:

$$(1)\ CH_2=CH—CH_2—Br + Mg \rightarrow CH_2=CH—CH_2MgBr$$

$$(2)\ CH_2=CH—CH_2MgBr + RCHO \rightarrow CH_2=CH—CH_2—CH(OH)—R$$

$$(3)\ CH_2=CH—CH_2—CH(OH)—R + NaHSO_3 \rightarrow NaSO_3—CH_2—CH_2—CH_2—CH(OH)—R$$

(R is a long chain alkyl radical)

In some case, a long-chain α-olefine may be employed as a raw material, and gaseous sulphur trioxide is diluted with gas and continuously sulphonated by a falling film type reactor. The sulphonated mixture containing 1—3 and 1—4 sulphone is hydrolized with caustic alkali to produce a mixture of 3-hydroxyalkanesulphonate and 4-hydroxyalkanesulphonate with high yield.

The methods which may be used to obtain 3-hydroxyalkanesulphonate and/or 4-hydroxyalkanesulphonate are not limited by the above.

The hydroxysulphonates used for this invention are superior to other sulphonates because of their solubility to water.

Particularly, 3-hydroxyalkanesulphonates and 4-hydroxyalkanesulphonates are preferable because of their excellent water-solubility. This occurs because they have no hydrogen-bond between the —SO_3M and —OH radicals and, thus, both radicals act as hydrophillic agents to increase the solubility. Compared with these sulphonates, 2-hydroxyalkanesulphonates do not have sufficient water-solubility, although they belong to this group of sulphonates, and have a poor foaming effect when used in dentifrice; it has been found that the 2-hydroxysulphonates are not suitable for the dentifrices of the invention.

To the dentifrice composition of the present invention, the usually-employed foaming agents, such as alkylsulphates, acylsarcosinates, hydroxyalkylsulphates, fatty acid alkylol amides, fatty acid monoglyceride sulphates and acyl taurates may be added.

The hydroxyalkanesulphonate is preferably addedy in the amount of 0.1%—10% by weight, preferably 0.5—3% by weight, based on the dentifrice base consisting of dentifrice-effective components. When the added amount exceeds 10% by weight, the solubility of the foaming agent is reduced considerably, and when the added amount is less than 0.1% by weight, the foaming effect and the Orange Juice effect are apt to deteriorate: consequently, it is preferable for the added amount not to be outside the prescribed range of 0.1%—10%.

The dentifrice composition of the present invention can be prepared as a tooth powder, a toothpaste or a powder suitable for forming into a tooth paste.

The hydroxyalkanesulphonate used in the present invention added to the dentifrice base gives a good foaming effect and produces fine, tough and stable foams which yield a good palatability by retaining the flavour on the mucous membrane in the mouth. It also gives a good Orange Juice effect, which may perhaps be due to the existence and the position of the hydroxy group in the hydrophilic group, though partly depending on the properties of the structure of the active agent of the hydroxyalkanesulphonate.

The following Table 2 shows the results of sensory tests on a dentifrice composition of the present invention, as compared with compositions containing either only an ordinarily used alkylsulphate or acylsarcosinate foaming agent:

TABLE 2

	When using		After using	
	Foaming	Taste	Orange Juice effect	Stimulation to the mucous membrane
Dentifrice containing alkylsulphate	Good	Good	Poor	Good
Dentifrice containing acylsarcosinate	Fair	Slightly bitter	Good	Stomatitis-like symptom recognized
Dentifrice of the present invention	Excellent	Good	Good	Good

As can be seen from this Table, when a dentifrice of the present invention is used, the Orange juice effect is markedly improved and the defects of ordinarily used foaming agents can be easily reduced. The acylsarcosinate agent is inferior in foaming effect and has too strong a stimulation on the mucous membrane in the mouth. If a large amount of this substance is blended in a dentifrice, there will be a danger of burning of the mucous membrane in the mouth after using it. By means of the present invention, these defects are reduced, and the foaming effect is better than with an alkyl sulphate additive. The dentifrice of the invention is also free from uncomfortable bitterness which sometimes occurs with fatty acid monoglyceridesulphates. Furthermore, the dentifrice of the present invention produces abundant fine and stable foams which greatly increase the cleaning activity in the mouth and, due to its excellent foaming effect, stimulation is much less than with many ordinary products. It is also satisfactory in giving a refreshing palatability during and after using.

The Examples of dentifrices of the present invention will now be given:

EXAMPLE 1

Tooth paste:—	
Dibasic calcium phosphate	50.0
Glycerin	30.0
Na-carboxymethylcellulose	1.0
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxytetradecane-sulphonate	2.0
Water	15.9
	100.0% by weight

EXAMPLE 2

Tooth paste:—	
Dibasic calcium phosphate	50.0
Glycerine	30.0
Na-carboxymethylcellulose	1.0
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxyhexadecanesulphonate	1.5
Na-laurylsulphate	0.5
Water	15.9

100.0% by weight

EXAMPLE 3

Tooth paste:—	
Dibasic calcium phosphate	50.0
Glycerine	30.0
Na-carboxymethylcellulose	1.0
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxytetradecanesulphonate or Na - 4 - hydroxytetradecanesulphonate	1.5
Na-lauroylsarcosinate	0.5
Water	15.9

100.0% by weight

EXAMPLE 4

Tooth Paste:—	
Calcium carbonate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Mixture of Na - 3 - hydroxytetradecanesulphonate and 4 - hydroxytetradecanesulphonate	1.5
Water	21.2

100.0% by weight

EXAMPLE 5

Tooth paste:—	
Dibasic calcium phosphate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxyhexadecanesulphonate	1.0
Na-Laurol monoglyceride sulphate	1.0
Water	20.2
Lauroyldiethanolamide	0.5

100.0% by weight

EXAMPLE 6

Tooth paste:—	
Calcium carbonate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxydecanesulphonate	1.5
Lauroyldiethanolamide	0.5
Water	20.7

100.0% by weight

EXAMPLE 7

Tooth paste powder:—	
Calcium carbonate	75.0
Glycerine	10.0
Saccharin	0.1
Flavouring Agent	0.8
Na - 3 - hydroxyhexadecanesulphonate / Na - 4 - hydroxyhexadecanesulphonate mixture	1.0
Water	13.1

100.0% by weight

EXAMPLE 8

Tooth paste powder:—	
Calcium carbonate	75.0
Glycerine	10.0
Saccharin	0.1
Flavouring Agent	0.8
Na - 3 - hydroxytetradecanesulphonate or Na - 4 - hydroxytetradecanesulphonate	1.0
Na-laurylsulphate	0.5
Water	12.6

100.0% by weight

WHAT WE CLAIM IS:—

1. A dentifrice composition comprising at least one water-soluble hydroxyalkanesulphonate in a dentifrice base.

2. A dentifrice composition as claimed in claim 1, in which the hydroxyalkanesulphonate is a 3-hydroxyalkanesulphonate or a 4-hydroxyalkanesulphonate or a mixture thereof.

3. A dentifrice composition as claimed in claim 1 or claim 2, in which the total amount of hydroxyalkanesulphonate in the composition is in the range 0.1 to 10% by weight, based on the weight of dentifrice base.

4. A dentifrice composition as claimed in claim 3, in which the said amount of hydroxyalkanesulphonate is in the range 0.5% to 3%.

5. A dentifrice composition as claimed in any preceding claim in which the or each hydroxyalkanesulfonate group contains 12 to 24 carbon atoms.

EXAMPLE 2

Tooth paste:—	
Dibasic calcium phosphate	50.0
Glycerine	30.0
Na-carboxymethylcellulose	1.0
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxyhexadecanesulphonate	1.5
Na-laurylsulphate	0.5
Water	15.9

100.0% by weight

EXAMPLE 3

Tooth paste:—	
Dibasic calcium phosphate	50.0
Glycerine	30.0
Na-carboxymethylcellulose	1.0
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxytetradecanesulphonate or Na - 4 - hydroxytetradecanesulphonate	1.5
Na-lauroylsarcosinate	0.5
Water	15.9

100.0% by weight

EXAMPLE 4

Tooth Paste:—	
Calcium carbonate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Mixture of Na - 3 - hydroxytetradecanesulphonate and 4 - hydroxytetradecanesulphonate	1.5
Water	21.2

100.0% by weight

EXAMPLE 5

Tooth paste:—	
Dibasic calcium phosphate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxyhexadecanesulphonate	1.0
Na-Laurol monoglyceride sulphate	1.0
Water	20.2
Lauroyldiethanolamide	0.5

100.0% by weight

EXAMPLE 6

Tooth paste:—	
Calcium carbonate	45.0
Sorbitol solution	30.0
Irish moss gum	1.2
Flavouring Agent	1.0
Saccharin	0.1
Na - 3 - hydroxyhexadecanesulphonate or Na - 4 - hydroxydecanesulphonate	1.5
Lauroyldiethanolamide	0.5
Water	20.7

100.0% by weight

EXAMPLE 7

Tooth paste powder:—	
Calcium carbonate	75.0
Glycerine	10.0
Saccharin	0.1
Flavouring Agent	0.8
Na - 3 - hydroxyhexadecanesulphonate / Na - 4 - hydroxyhexadecanesulphonate mixture	1.0
Water	13.1

100.0% by weight

EXAMPLE 8

Tooth paste powder:—	
Calcium carbonate	75.0
Glycerine	10.0
Saccharin	0.1
Flavouring Agent	0.8
Na - 3 - hydroxytetradecanesulphonate or Na - 4 - hydroxytetradecanesulphonate	1.0
Na-laurylsulphate	0.5
Water	12.6

100.0% by weight

WHAT WE CLAIM IS:—

1. A dentifrice composition comprising at least one water-soluble hydroxyalkanesulphonate in a dentifrice base.

2. A dentifrice composition as claimed in claim 1, in which the hydroxyalkanesulphonate is a 3-hydroxyalkanesulphonate or a 4-hydroxyalkanesulphonate or a mixture thereof.

3. A dentifrice composition as claimed in claim 1 or claim 2, in which the total amount of hydroxyalkanesulphonate in the composition is in the range 0.1 to 10% by weight, based on the weight of dentifrice base.

4. A dentifrice composition as claimed in claim 3, in which the said amount of hydroxyalkanesulphonate is in the range 0.5% to 3%.

5. A dentifrice composition as claimed in any preceding claim in which the or each hydroxyalkanesulfonate group contains 12 to 24 carbon atoms.

6. A dentifrice composition as claimed in any preceding claim in which the cations of the water-soluble hydroxyalkanesulphonate or hydroxyalkanesulphonates are an alkali metal or alkaline earth metal, ammonium or alkanolamine.

7. A dentifrice composition as claimed in any preceding claim in which the hydroxyalkanesulphonate is sodium 3-hydroxytetradecanesulphonate or sodium 4-hydroxytetradecanesulphonate or sodium 3-hydroxydecanesulphonate or sodium 4-hydroxyhexadecanesulphonate or a mixture of two or more of these.

8. A dentifrice composition as claimed in claim 1 substantially as herein described or given in any of Examples 1 to 8.

9. A process for the preparation of a dentifrice composition characterized by mixing a water-soluble 3-hydroxyalkanesulphonate and/or 4-hydroxyalkanesulphonate with a dentifrice base containing a polishing agent, a flavouring agent, a sweetener and water.

STANLEY, POPPLEWELL, FRANCIS & ROSS,
Agents for the Applicants,
20/21 Tooks Court,
Cursitor Street,
London, EC4A 1LB.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

