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[54] **DETERGENT COMPOSITION CONTAINING HYDROGENATED ALPHA OLEFIN SULFONATES**

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Related U.S. Application Data

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[52] **U.S. Cl.** **252/535,** 252/536, 252/554, 252/555

[51] **Int. Cl.** **C11d 3/065,** C11d 1/12

[58] **Field of Search**.....252/161, 138, 137, 536, 555; 260/513

[56] **References Cited**

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[57] **ABSTRACT**

High performance detergent compositions consist of straight-chain hydrogenated olefin sulfonates, an alkali metal or ammonium group pentavalent phosphoric acid salt and an alkanol-l.

7 Claims, No Drawings

DETERGENT COMPOSITION CONTAINING HYDROGENATED ALPHA OLEFIN SULFONATES

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of application Ser. No. 685,948, filed Nov. 27, 1967, now U.S. Pat. No. 3,565,809.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is concerned with the field of biodegradable sulfonate detergents and more particularly with readily biodegradable olefin sulfonates having improved detersive characteristics.

2. Prior Art

Because of the importance of biodegradability, linear alkylbenzene sulfonates now comprise the major active ingredient of household detergents. Although olefin sulfonates are more biodegradable than linear alkylbenzene sulfonates, heretofore, they have not been comparable in terms of detersive characteristics.

The present invention provides novel, readily biodegradable, high performance olefin sulfonate detergent compositions suitable for replacing linear alkylbenzene sulfonates.

SUMMARY OF THE INVENTION

Unexpectedly, it has now been found that ternary mixtures of olefin sulfonates containing 11 to 19 carbon atoms, alkali metal or ammonium group pentavalent phosphoric acid salts and alkanol-1 compounds containing 10 to 15 carbon atoms selected from the normal and 2-methyl isomers possess unusually high detersive characteristics. In particular, the performance of the described ternary mixtures is significantly greater than would be predicted from a knowledge of the performance of the corresponding binary mixtures or of the components individually. The mechanism by which the olefin sulfonates, alkali pentavalent phosphoric acid salts and alkanols cooperate or interact to produce the improved detersive characteristics is unknown. It is known, however, that all three components are necessary to produce the beneficial effects.

The term "olefin sulfonates" as used in the present invention represents a composition consisting of from 50–100 percent unsaturated olefin sulfonates. When the unsaturated olefin sulfonate portion is below approximately 100 percent, the balance of the composition comprises substantially hydroxy sulfonates. Other compounds may also be present in minor amounts due to impurities in olefin feedstock or as the result of sulfonation side reactions. The relative proportions of hydroxy and unsaturated sulfonate will vary depending upon the method of preparation. That is, for example, by one method as described in Turbak, A. F. et al., "Reaction of Phosphate-Complex Sulfur Trioxide with Alpha-Olefins," Industrial and Engineering Chemistry, Product Research and Development 2, No. 3, 229 (1963), an olefin sulfonate comprising substantially 100 percent unsaturated olefin sulfonate may be prepared.

Usually, the amount of hydroxy sulfonate will range from 0 to 50 percent by weight of the total olefin sulfonates, and preferably less than 40 percent. The unsaturated sulfonates may range from 50 to 100 percent by weight of total olefin sulfonates. Preferably the unsaturated sulfonates comprise more than 60% of the total olefin sulfonates.

Olefin sulfonates of the present invention are prepared by sulfonation of straight-chain or normal olefins containing 10 to 24 carbon atoms, usually 11 to 19 carbon atoms and preferably containing 15 to 18 carbon atoms. Single carbon cuts of olefins within this range may also be employed, for example, hexadecene-1. The olefins may be internal or alpha olefins, although alpha olefins are preferred. Sulfonation may be accomplished by any suitable process which produces the proper range of hydroxy and unsaturated sulfonates.

The preferred method of preparation of olefin sulfonates comprises SO_3-air sulfonation in a falling film reactor, neutralization and saponification or hydrolysis of the neutralized product. The reaction products of the SO_3-air sulfonation step may be neutralized with an aqueous alkali solution containing any strongly basic compound such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, the corresponding oxides, carbonates and the like. Sufficient neutralizing solution is added to provide for the subsequent hydrolysis step. Hydrolysis of the neutralized reaction products yields the olefin sulfonates as defined in the present invention.

Generally, the sulfonation conditions cause migration of the double bond in the unsaturated sulfonates and determine the distribution of the double bond locations. Analysis of an alpha olefin C_{15}–C_{18} carbon cut sulfonated with SO_3-air and suitable for use in the present invention is illustrated in Table I.

TABLE I

Composition of product, after saponification	
Alkene sulfonates, %[a]	53
Hydroxy sulfonates, %[a]	47
$RCH{=}CH{-}(CH_2)_xSO_3Na$	
x	Mole %
0	9
1	21
2	16
3	5
4	6
5	6
6	7
7	6
8	7
9	8
10	9

[a]Includes disulfonates

Sulfonation also produces a variety of hydroxy sulfonate isomers. Since the beta or 2-hydroxy sulfonates are to some degree insoluble in water, processes which minimize their formation are preferred. A suitable process is described in Marquis et al., *Alpha Olefin Sulfonates from a Commercial SO_3 Reactor*, JAOCS, Volume 43, No. 11, pp. 607–614 (1966). British Pat. No. 1,030,648 describes another sulfonation process which may be utilized.

Olefin sulfonates prepared in accordance with the present invention may be modified by mild hydrogenation to produce hydrogenated olefin sulfonates. Hydrogenated olefin sulfonates alone or in mixtures with olefin sulfonates provide excellent active com-

ponents suitable for the present invention. Hydrogenation of the olefin sulfonates substantially reduces all of the unsaturated sulfonates to alkane sulfonates with little or no effect on the hydroxy sulfonates. The hydrogenation may be conducted with hydrogen at a pressure of 50–800 psig, at a temperature of 45°–80°C. for 60 minutes over 5% Pd on carbon or barium sulfate as a catalyst.

The primary alkanol component of the detergent composition contains 10 to 15 carbon atoms. The preferred alkanols have the normal or the 2-methyl isomer configuration. Suitable alcohols include decanol-1, undecanol-1, dodecanol-1, tridecanol-1, tetradecanol-1, pentadecanol-1, 2-methyl nonanol, 2-methyl decanol-1, 2-methyl undecanol-1, 2-methyl dodecanol-1, 2-methyl tridecano-1, and 2-methyl tetradecanol. The preferred alkanols may be added separately or in any combination, for example, 75 percent dodecanol-1 and 25 percent 2-methyl dodecanol-1.

The suitable pentavalent phosphoric acid salts include the tripolyphosphates, pyrophosphates, metaphosphates and orthophosphates. The cation portion of the phosphates may be sodium, potassium, ammonium and the like. For example, suitable phosphates would include, but are not limited to: sodium tripolyphosphate, potassium tripolyphosphate, ammonium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, trisodium phosphate, tripotassium phosphate, ammonium phosphate, sodium hexametaphosphate, potassium hexametaphosphate, ammonium hexametaphosphate, monosodium orthophosphate, monopotassium orthophosphate, disodium orthophosphate, dipotassium orthophosphate and the like.

The ternary mixtures of the present invention may be prepared in the usual manner known in the art. The order of combining the ingredients is immaterial. The mixtures so prepared may be utilized as effective detergents if desired. Preferably, however, the detergent compositions of the present invention are incorporated with other ingredients into detergent formulations.

The prescribed quantity of surface active ingredient present in a detergent formulation generally constitutes from about 15 to 35 percent by weight of the total detergent formulation. The olefin sulfonates of the present invention may likewise be utilized in the same concentrations, although preferably from 15 to 25 percent. Correspondingly, the amount of olefin sulfonate employed in a detergent formulation will determine the range of the pentavalent phosphoric acid salt and alkanol-1.

An effective amount of alkali pentavalent phosphoric acid salt usually comprises from about one-fourth to 3 parts by weight per part of olefin sulfonate. Preferably, the ratio is 1 to 2 parts by weight per part of olefin sulfonate.

The selected alkanols or mixtures thereof may comprise from about 4 to 40 parts by weight per hundred parts of olefin sulfonate. The most desirable ratio is usually from 8 to 30 parts by weight per hundred parts of olefin sulfonate.

Additional compatible ingredients may be incorporated into the detergent compositions prepared in accordance with the present invention to enhance their detergent properties. Such ingredients may include, but are not limited to, anticorrosion, antiredeposition, chemical bleaching and sequestering agents; optical whiteners and certain inorganic salts other than phosphate, such as inorganic sulfates, carbonates or borates. The appropriate quantities and compositions of these additives, agents and builders are well described in the art.

An effective means for evaluating the detersive characteristics of detergent compositions is known as the "Hand Dishwashing Test" which is based on a procedure presented at the ASTM D–12 subcommittee on Detergents, mar. 10, 1949, New York N.Y. The test measures under simulated home washing conditions the number of plates or dishes washed before the foam collapses. This test was utilized to evaluate the improved performance of the disclosed detergent compositions.

Detergent formulations were prepared from the ternary mixtures of the present invention by the addition of water alone or with other ingredients. The formulations were adjusted until the percentage of alcohol and olefin sulfonate equalled 25 percent by weight of the total detergent formulation.

In the following examples, the concentrations employed in the "Hand Dishwashing Test" were 0.15 percent by weight of the total detergent formulation.

EXAMPLE 1 illustrates a suitable detergent formulation prepared EXAMPLE the ternary mixtures of the present invention.

EXAMPLE 1

A detergent formulation was prepared containing the following percentages of each ingredient, based on the total weight of the formulation:

	Formulation %	Ternary Mixture %
Alpha olefin (C_{15}–C_{18}) sulfonate	21	32
sodium tripolyphosphate	40	62
dodecanol-1	4	6
sodium silicate	7	
carboxy methylcellulose	1	
sodium sulfate	19	
water	8	

The formulation was tested and found effective in accordance with the "Hand Dishwashing Test" for a rating of 24 plates.

The data presented in Table II illustrates the relative dishwashing ability of olefin sulfonates individually and in binary mixtures with phosphate and alkanol-1. The presence of the phosphate appears to exert a substantial negative effect on the dishwashing ability of the olefin sulfonates.

TABLE II

Mixture Composition in Weight %

Example	Phosphate	Sulfonate[1]	Dodecanol-1	Plates[2]
2	0	100	0	20
3	0	84	16	20
4	28[3]	62	0	18
5	44[3]	56	0	17
6	62[3]	38	0	15
7	62[4]	38	0	18
8	62[5]	38	0	18
9[6]	71[5]	29	0	17

[1]Alpha olefin sulfonate C_{15}–C_{18} carbon cut

[2]As measured by "Hand Dishwashing Test"
[3]Sodium tripolyphosphate
[4]Trisodium phosphate
[5]Tetrasodium pyrophosphate
[6]Includes inert builders such as sodium silicate, carboxy methyl-cellulose and sodium sulfate

Tables III and IV represent data obtained from formulations containing all three components. Both tables illustrate the importance of alcohol concentrations on dishwashing ability.

TABLE III

Ternary Mixture Composition in Weight %

Example	Phosphate[1]	Sulfonate[2]	Dodecanol-1	Plates[3]
10	28	52	10	22
11	44	37	9	24
12	62	32	6	23

[1]Sodium tripolyphosphate
[2]Alpha olefin sulfonate C_{15}–C_{18} carbon cut
[3]As measured by "Hand Dishwashing Test"

TABLE IV

Ternary Mixture Composition in Weight %

Example	Phosphate[1]	Sulfonate[2]	Dodecanol-1	Plates[3]
13	62	26	12	15
14	62	28	10	20
15	62	32	6	24
16	62	35	3	22

[1]Tetrasodium pyrophosphate
[2]Alpha olefin sulfonate C_{15}–C_{18} carbon cut
[3]As measured by "Hand Dishwashing Test"

The changes produced in the dishwashing ability of the present compositions by varying the carbon chain length of the alkanol are shown in Table V.

TABLE V

Example	n-Alkanol[1] (No. of Carbon Atoms)	Plates
17	8	16
18	10	23
19	11	24
20	12	24
21	13	23
22	14	21
23	16	15

[1]Ternary mixture composition: phosphate 61%; alkanol 6%, olefin sulfonate 33%

The dishwashing ability of formulations containing various alcohols is compared with those of the present invention in Table VI

TABLE VI

Example	Alcohol[1]	Plates
24	Primary C_{13}–C_{15} "oxo" alcohols containing 70–80% straight chain material	24
25	2-methyl dodecanol-1	24
26	4- and 6-methylol dodecane	15
27	41 and 6-methylol undecane	15
28	C_{14} oxo alcohol 30% straight chain	17
29	C_{13} branched oxo alcohol	18
30	mixed secondary dodecanols	15
31	mixed secondary tetradecanols	15

[1]Ternary mixture composition; alcohol 6%; phosphate 61%; olefin sulfonate 33%

Table VII illustrates the dishwashing ability of formulations containing hydrogenated olefin sulfonate alone and in mixtures with olefin sulfonates as the major active components.

TABLE VII

Ternary Mixture Composition in Weight %[1]

Example	Dodecanol-	Hydrogenated Olefin Sulfonate	Olefin Sulfonate	Plates
32	0	38	0	25
33	6	32	0	31
34	0	19	19	23
35	6	16	16	28

[1]62% phosphate

As will be evident to those skilled in the art, various modifications on this process can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

I Claim:

1. A detergent composition having improved detersive characteristics consisting essentially of

normal alkali metal and ammonium hydrogenated olefin sulfonates produced by sulfonating straight-chain olefines containing 11 to 19 carbon atoms with SO_3, neutralizing the resulting mixture with an alkali metal or ammonium hydroxide, carbonate or oxide, hydrolyzing the neutralized product, and subsequently hydrogenating the hydrolyzed product to substantially reduce all of the unsaturated olefin sulfonates to alkane sulfonates, said hydrogenated product consisting essentially of a mixture of alkane and hydroxy alkane sulfonates,

an alkali metal or ammonium pentavalent phosphoric acid salt in a ratio of about one-fourth to 3 parts per part by weight of sulfonate, and

an alkanol-1 containing 10 to 15 carbon atoms selected from the class consisting of the normal and 2-methyl isomers in a ratio of about 4 to 40 parts per hundred parts by weight of sulfonate.

2. A detergent composition according to claim 1, wherein the alkanol-1 is dodecanol-1.

3. A detergent composition according to claim 2, wherein the phosphoric acid salt is selected from the group consisting of sodium tripolyphosphate, tetrasodium pyrophosphate and trisodium phosphate.

4. A detergent composition according to claim 3, wherein the phosphoric acid salt is present in a ratio of about 1 to 2 parts per part by weight of sulfonate.

5. A detergent composition according to claim 4, wherein the alkanol-1 is present in a ratio of about 8 to 30 parts per hundred parts by weight of sulfonate.

6. A detergent composition according to claim 5, wherein the alkanol-1 is composed of a mixture of the normal and 2-methyl isomers.

7. A detergent composition according to claim 5, wherein the hydrogenated olefin sulfonate is derived from an alpha olefin cut containing 15 to 18 carbon atoms.

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