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3,565,809

ALPHA OLEFIN SULFONATE
DETERGENT COMPOSITIONS

Samuel H. Sharman, Kensington, Calif., assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

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8 Claims

ABSTRACT OF THE DISCLOSURE

High performance detergent compositions consist of straight-chain olefin sulfonates, an alkali metal or ammonium group pentavalent phosphoric acid salt and an alkanol-1.

BACKGROUND OF THE INVENTION

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 deterative characteristics.

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 deterative 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 deterative 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 deterative 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% unsaturated olefin sulfonates. When the unsaturated olefin sulfonate portion is below approximately 100%, 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-Complexed Sulfur Trioxide With Alpha-Olefins," Industrial and Engineering Chemistry, Product Research and Development 2, No. 3, 229 (1963), an olefin sulfonate comprising substantially 100% unsaturated olefin sulfonate may be prepared.

Usually, the amount of hydroxy sulfonate will range from 0 to 50% by weight of the total olefin sulfonates,

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and preferably less than 40%. The unsaturated sulfonates may range from 50 to 100% 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 SO₃-air sulfonation in a falling film reactor, neutralization and saponification or hydrolysis of the neutralized product. The reaction products of the SO₃-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 C₁₅-C₁₈ carbon cut sulfonated with SO₃-air and suitable for use in the present invention is illustrated in Table I.

TABLE I

Composition of product, after saponification

Alkene sulfonates, percent ^a	53
Hydroxy sulfonates, percent ^a	47
RCH=CH-(CH ₂) _x SO ₃ Na	—

^a Includes disulfonates.

^b See the following table:

x :	Mole percent
0	9
1	21
2	16
3	5
4	6
5	6
6	7
7	6
8	7
9	8
10	9

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 SO₃ Reactor, IAOCS, 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 components 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 p.s.i.g., 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 tridecanol-1, and 2-methyl tetradecanol. The preferred alkanols may be added separately or in any combination, for example, 75% dodecanol-1 and 25% 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% 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%. 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 1/4 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 deterative characteristics or 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% by weight of the total detergent formulation.

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

Example 1 illustrates a suitable detergent formulation prepared from 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, percent	Ternary mixture, percent
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 PERCENT

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

¹ Alpha olefin sulfonate C₁₅-C₁₈ 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 PERCENT

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

¹ Sodium tripolyphosphate.

² Alpha olefin sulfonate C₁₅-C₁₈ carbon cut.

³ As measured by "Hand Dishwashing Test."

TABLE IV.—TERNARY MIXTURE COMPOSITION IN WEIGHT PERCENT

	Phosphate ¹	Sulfonate ²	Dodecanol-1	Plates ³
Example:				
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 C₁₅-C₁₈ 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.

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TABLE V

	n-Alkanol ¹ , number of carbon atoms	Plates
Example		
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

	Alcohol ¹	Plates
Example:		
24-----	Primary C ₁₂ -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-----	4- 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 PERCENT¹

	Dodec- anol-1	Hydro- genated olefin sulfo- nate	Olefin sulfo- nate	Plates
Example:				
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.

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I claim:

1. A detergent composition having improved deter-
sive characteristics consisting essentially of
normal alkali metal or ammonium olefin water-soluble
sulfonates containing 11 to 19 carbon atoms,
a pentavalent phosphoric acid alkali metal or ammo-
nium salt in a ratio of about ¼ 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, where-
in the phosphoric acid salt is selected from the group
consisting of sodium tripolyphosphate, tetrasodium py-
rophosphate and trisodium phosphate.
4. A detergent composition according to claim 3, where-
in the phosphoric acid salt is present in a ratio of about
1 to 2 parts by part of sulfonate.
5. A detergent composition according to claim 4, where-
in 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, where-
in the alkanol-1 is composed of a mixture of the nor-
mal and 2-methyl isomers.
7. A detergent composition according to claim 5, where-
in the olefin sulfonate is derived from an alpha olefin
cut containing 15 to 18 carbon atoms.
8. A detergent composition according to claim 7, where-
in the olefin sulfonate comprises a mixture of hydrogen-
ated olefin sulfonates and olefin sulfonates.

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LEON D. ROSDOL, Primary Examiner

P. E. WILLIS, Assistant Examiner

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