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2,995,524

DETERGENT COMPOSITIONS

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This invention relates to detergent compositions and more particularly to a combination of two detergents which together form a new composition having unexpected special properties that render it especially valuable for particular applications such as those mentioned hereinafter.

It is well known that excellent detergents can be obtained by sulfonating alkyl benzene type materials which contain 9-15 carbon atoms in the alkyl group. Such products, neutralized with appropriate bases, are sold to some extent as liquid detergents but are usually mixed with some kind of builder and dried. Detergents of this type have many very desirable properties, but for certain particular applications their use is accompanied by known disadvantages.

A recent patent (U.S. Patent No. 2,743,288) describes a new type of surface active agent, a monosulfonated oleic acid, which has unique properties in such applications as crystallization operations and polymerization emulsions, and as an antifothing agent in acidulation of mineral ores. As described in the aforesaid patent, the sulfonation of oleic acid results in a product that is still monocarboxylic and predominantly unsaturated and that contains approximately one mole of combined SO₃ per mole of oleic acid. We have discovered quite unexpectedly that the addition of such oleic acid monosulfonates to dodecylbenzenesulfonates produces compositions which substantially eliminate the aforesaid known disadvantages of alkyl benzene sulfonates and provide improved properties for certain applications. Such compositions, for instance, have lower cloud points than the dodecylbenzenesulfonate alone. Compositions containing the free acids of these two sulfonated products are especially valuable in the textile and allied industries since such concentrated acids can be stored and handled in the minimum of space and with the minimum of difficulty. These acids can then be neutralized as needed with the desired base. The resulting detergent solutions have unusually good tolerance for alkaline builders and are more effective surface active agents in some electrolyte solutions than either component alone.

Still another advantage of such compositions is realized when they are dried with major amounts of inorganic salts and builders. Ordinarily such mixtures, containing say 40% sodium dodecylbenzenesulfonate and 60% sodium sulfate, present severe dusting problems with resulting loss of material, expensive recovery problems and health hazards. We have found, however, that sodium dodecylbenzenesulfonate, for example, containing 10-50% of sodium oleic acid monosulfonate, can be dried with one and one-half times its weight of sodium sulfate without the usual dusting problems. In such cases the dried product will contain say 60% sodium sulfate and 40% of a mixture in the proportions of 20-36% sodium dodecylbenzenesulfonate and 20-4% sodium oleic acid monosulfonate.

Whether the detergent mixture is to be stored as a mixture of the two detergent acids for neutralization and use as needed, or is to be neutralized and drum dried with inorganic builders, the two acids should be mixed in the proportions of 10-50 parts of oleic acid monosulfonate

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and 90-50 parts dodecylbenzenesulfonic acid. The two acids can be prepared separately and mixed together in any suitable manner. It may be preferred, however, to sulfonate the dodecylbenzene with sulfur trioxide dissolved in liquid sulfur dioxide, and then to provide the desired amount of the oleic acid monosulfonate of U.S. Patent No. 2,743,288 by adding oleic acid for sulfonation in a second stage addition of the sulfur trioxide-sulfur dioxide. The resulting mixtures of detergent acids have approximately the same composition and properties when prepared in either manner.

The following examples will illustrate the invention and its advantages:

(A) The dodecylbenzenesulfonic acid was manufactured by the sulfonation of a commercial grade of dodecylbenzene. The acid was composed of approximately:

92.5% dodecylbenzenesulfonic acid
1.5% unsulfonated oils
1.5% sulfuric acid
4.5% water

(B) The sulfonated oleic acid was manufactured by sulfonating a commercial grade of oleic acid by the process described in U.S. Patent No. 2,743,288. This acid had the following composition:

61.8% sulfonated fatty acid
25.0% water
8.6% unsulfonated fatty acid
4.6% sulfuric acid

Blends of these two acids were made and the following data were obtained on these products:

COMPOSITIONS		
Detergent acid mixture—Sample No.	Parts acid "A"	Parts acid "B"
1	80	20
2	70	30
3	60	40

CLOUD POINTS		
Detergent acid mixture—Sample No.	Percent acid (sodium salt, pH 10)	Cloud point, ° C.
1	35	25.8
2	35	24.2
3	35	23.5

WETTING TIMES IS SECONDS AT 80° F. (CLARKSON-DRAVES)				
Detergent acid mixture—Sample No.	Percent acid (sodium salt, pH 10)	In H ₂ O	In 2% NaOH	In 2% H ₂ SO ₄
1	.1	6.1	20	6
2	.1	7.3	16.8	6
3	.1	9.3	11.5	9.6

ROSS-MILES FOAM HEIGHTS			
Detergent acid mixture—Sample No.	Concentration of acid (as sodium salt, pH 10)	Foam height in cm.	
		Initial	After 5 Min.
1	.1	15	14.5
2	.1	16	16
3	.1	15	14.5

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Generally speaking, dodecylbenzenesulfonic acid is the better and cheaper detergent of the two acids when used separately, but the addition of the oleic acid monosulfonate imparts solubilizing effects to the mixture and provides improved wetting properties in alkaline solution. The properties of the above samples in distilled water and acid are only slightly affected by variations in the amount of oleic acid monosulfonate. In distilled water, for example, the wetting power gradually falls off somewhat as the amount of oleic acid monosulfonate is increased from Sample 1 to Sample 3. In acid, the wetting power remains the same for Samples 1 and 2, but falls off somewhat for Sample 3. In alkaline solution, on the other hand, the wetting power increases very materially, the time for Sample 3 being reduced nearly to half that for Sample 1.

These detergent acid mixtures can be conveniently neutralized with appropriate bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, and triethanolamine. This is best accomplished by first diluting the acid to approximately 40-50% with water and then adding the concentrated base to this solution.

These mixed detergents have outstanding ability to tolerate high concentrations of inorganic alkaline salts used as builders and the like. For instance, the following typical formulas can be prepared for use in the textile field and as heavy duty liquid detergents:

I

200 parts Sample No. 2 detergent acid mixture
672 parts water
52 parts 50% sodium hydroxide
100 parts trisodium phosphate

The cloud point for this formula is 25.8° C., whereas if acid A alone is used instead of the mixture, the cloud point is 86° C.

II

200 parts Sample No. 2 detergent acid mixture
672 parts water
52 parts 50% sodium hydroxide
100 parts sodium tripolyphosphate

The cloud point for this formula is 25.3° C., whereas when acid A alone is used instead of the mixture, the cloud point is 73° C.

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III

150 parts Sample No. 3 detergent acid mixture
766 parts water
39 parts 50% sodium hydroxide
70 parts soda ash

This formula has a cloud point of 26.1° C., but when acid A alone is used in place of the mixture, the cloud point is 91° C.

It should be apparent that such mixtures as we have described possess valuable and useful properties.

What is claimed is:

1. A detergent composition consisting essentially of a mixture of (A) a member selected from the group consisting of neutralized and unneutralized dodecylbenzenesulfonic acid and (B) a member selected from the group consisting of neutralized and unneutralized sulfonated oleic acid that is monocarboxylic and predominantly unsaturated and contains approximately one mole of combined SO₃ per mole of oleic acid in the proportions of 10-50 parts of (B) to 90-50 parts of (A).

2. A detergent composition consisting essentially of 10-50 parts of sulfonated oleic acid that is monocarboxylic and predominantly unsaturated and contains approximately one mole of combined SO₃ per mole of oleic acid and 90-50 parts of dodecylbenzenesulfonic acid.

3. A detergent composition consisting essentially of salts of dodecylbenzenesulfonic acid and sulfonated oleic acid that is monocarboxylic and predominantly unsaturated and contains approximately one mole of combined SO₃ per mole of oleic acid in the proportions of 90-50 parts of dodecylbenzenesulfonic acid to 10-50 parts of oleic acid monosulfonate, said salts being selected from the group consisting of alkali and ammonium salts of the sulfonic and carboxylic acids present in said composition.

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