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AQUEOUS DETERGENT

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This invention relates to detergents and more particularly to detergents comprising aqueous solutions of alkyl aryl sulfonates.

The use of detergent water-soluble alkali alkyl aryl sulfonates having long chain alkyl groups for cleaning purposes is quite well known. In accordance with such usage, said alkali sulfonates with or without builders are dissolved in water, and the aqueous solutions are used to clean fabrics, dishes, automobiles, and numerous other objects. By builders we mean additives which improve the performance of said sulfonates, preferably inorganic compounds which assist said sulfonates in their cleansing action, such, for example, as the various alkali phosphates and polyphosphates, alkali sulfates and the like.

These detergent sulfonates are quite effective in aqueous solutions at low concentrations, e. g., 0.2 to 0.4% by weight. However, for various purposes, inasmuch as such long chain alkali alkyl aryl sulfonates are relatively insoluble in water, the solubility being of the order of 2 to 3 per cent, and also because even this small amount of dissolved solids is precipitated in substantial amounts on temperature drops to but a few degrees, the utility of the aqueous solutions was not attractive for commercial exploitation.

It is an object of this invention to produce relatively concentrated aqueous detergent solutions of long chain alkali alkyl aryl sulfonates admixed with alkali sulfate builder which are stable to precipitation of a solid phase even at low temperatures.

It is also an object of this invention to produce relatively concentrated aqueous detergent solutions of long chain alkali alkyl aryl sulfonates admixed with alkali inorganic salt builder which yield clear solutions on transition from the frozen to the melted state.

It is also an object of this invention to produce relatively concentrated aqueous detergent solutions of long chain alkali alkyl aryl sulfonates that at normal room temperature contain greater amounts of dissolved sulfonate than is the normal solubility value and which may be used per se or as a diluted solution.

Other objects of this invention will become apparent from the following disclosure.

We have attained these objects by compounding water-soluble alkali alkyl aryl sulfonates having

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long chain alkyl groups, alkali sulfate (with or without additional builders), with various organic compounds, herein called solubilizers in conjunction with assistant solubilizers. By using our solubilizers and assistant solubilizers, not only are the detergent sulfonates dissolved in amounts to give normally supersaturated alkali alkyl aryl sulfonate-alkali sulfate solutions, but additional builders such as alkali pyrophosphate may be compatibly dissolved. Thus, we have also discovered that various builders such as tetra-alkali pyrophosphate and alkali carbonate may be solubilized along with our alkali inorganic sulfates, without substantially adversely affecting the final solution solubility characteristics, to yield a composition having desirable low temperature stability characteristics associated with improved cleaning characteristics.

The detergent sulfonates we prefer to use are of the long chain alkali alkyl aryl type, and more preferably those wherein the alkyl group contains 9 to 18 carbon atoms attached to the aryl, preferably benzene, nucleus by a primary, secondary or tertiary carbon atom. In the preferred form of our invention, we use long chain alkyl aryl sulfonates prepared by alkylating benzene with polymerized polypropylene of 9 to 18 carbon atoms. Subsequent sulfonation of this alkylate followed by neutralization with caustic yields a slurry containing a substantial amount of sodium sulfate builder. We have discovered that this slurry per se may be compounded in our composition, since it normally consists of about 50 per cent water and a mixture af alkali aryl sulfonate and alkali sulfate in a preferred ratio of about 3 parts of said sulfonate to about 2 parts of said sulfate by weight. However, independent addition of said alkali sulfonate and alkali sulfate as dry salts are within the contemplation of our invention. Furthermore, while we prefer a ratio of alkali alkyl aryl sulfonate to alkali sulfate of about 3 to 2, respectively, this is not a critical ratio and may vary considerably without deleteriously affecting our invention compositions.

The other builders such as the alkali salts of polyphosphates, preferably tetrasodium pyrophosphate, are not indispensable, but may be added for their sequestering effect toward iron and alkaline earth ions. Obviously, these sequestering compounds are more desirable in our

compositions whenever they are to be used in conjunction with hard waters possessing considerable amounts of dissolved alkaline earth and/or iron compounds. The addition of sequestering agents such as the various alkali polyphosphates may be dispensed with in our compositions, particularly as used in connection with cleaning and washing with soft waters.

We have also discovered that ammonium carbonate can be advantageously added to our alkali alkyl aryl sulfonate compositions containing alkali sulfate and alkali pyrophosphates. Ammonium carbonate addition, we have found, aids in buffering our ultimate compositions to yield a product slightly on the preferred alkaline pH side. However, our compositions, even though devoid of ammonium carbonate, are effective detergents and within the scope of our invention.

Our solubilizers are oxygen-containing alkylenes and preferably water soluble polyether alkylenes, such, for example, as monobutyl ethers of ethylene and propylene glycols and other short chain ethers of ethylene, polyethylene, propylene and polypropylene glycols. Such ethers as monobutyl ether of diethylene glycol, monoethyl ether of ethylene glycol, polyethylene glycols of molecular weights between 200 and 400, diethylene glycol and mixtures of the above and equivalent compounds are quite satisfactory. In general, monoethers of the mono-, di- and poly-ethylene glycols having less than 5 carbon atoms in the alkyl ether chain are preferred.

Our assistant solubilizers are water-soluble sulfonates of relatively low molecular weight, and preferably are alkali metal salts of sulfonated polyalkyl benzenes. Sulfonation products obtained from sulfur dioxide petroleum extracts and fractions thereof have been found to be very effective assistant solubilizers. Other highly water-soluble sulfonates may, however, be used in our compositions; for example, the alkali salts of tetrahydronaphthalene sulfonate are also very effective assistant solubilizers. Alkali sulfonates prepared from polyalkyl benzenes boiling within the range of 400° F. to 525° F. are preferred, especially so when obtained from petroleum extracts. Extract fractions and extracts obtainable from the sulfur dioxide extraction processes of mineral oil stocks, upon sulfonation and alkali neutralization, are very good assistant solubilizers, as they are substantially pure water-soluble polyalkyl benzene sulfonates.

The alkali sulfonates obtained from sulfur dioxide extract of petroleum are preferably prepared by extracting kerosene fractions with liquid sulfur dioxide, distilling the extract and taking the "cut" between 408° F. and 518° F. This "cut" is sulfonated with 96% clean sulfuric acid, and any acid formed is neutralized with alkali such as caustic or potash to form the corresponding sulfonate which product may be subsequently salted out of the mother liquor. A sulfonate prepared as above outlined had aromatic characteristics and contained about 20% water with traces of sodium chloride.

The extract "cut" (supra) prior to sulfonation had the following properties:

Flash point	°F.	200
Gravity	API	25.5
Sulfur content	per cent	0.20
Aniline point		30
Unsulfonatable residue	per cent	29
Initial boiling point	°F.	408
Final boiling point	°F.	518

In lieu of sodium petroleum sulfonates prepared from sulfur dioxide extract of petroleum, applicants have discovered that they may use sodium tetrahydronaphthalene sulfonate obtainable as Alkanol-S (Du Pont) with effective results.

These water-soluble sulfonates in some inexplicable manner improve our composition so as to bring about uniform re-solution of our frozen composition, thereby preventing the appearance of sediment. And by re-solution we mean the transition from the frozen solid state to the melted liquid state without the intermediate appearance of a separate solid salt phase. In short, our inventive compositions behave like eutectoid mixtures.

In proportioning the ingredients of our composition, account should be taken of the manner of addition of the water-soluble alkali alkyl aryl sulfonate and alkali sulfate, as these components as previously stated may be added separately or admixed in a dry state or as a mixed salt slurry with water. The amount of mixed salt slurry, comprising water-soluble alkali salt of long chain alkali alkyl aryl sulfonate admixed with alkali sulfate in the preferred ratio of about 3 to 2, respectively, and having about 50 per cent water which we may add, may vary from about 15 to about 25 per cent, and more particularly about 20 per cent of said slurry. This corresponds to from about 7.5% to about 12.5% and about 10% by weight, respectively, of the dry ingredients in the mixed salt slurry, based on the total composition of our invention.

Our inventive compositions may contain about 1 to about 5 per cent of oxygen-containing organic alkylene solubilizer such as monobutyl ether of ethylene glycol. However, about 2 to about 4 per cent is preferred and more specifically, we use about 3 per cent of said solubilizers.

The assistant solubilizers selected from the class consisting of alkali salts of sulfur dioxide extract petroleum sulfonates and alkali salts of tetrahydronaphthalene sulfonates we use in amounts varying from about one to about ten per cent of the composition by weight, and preferably in amounts of about 2 to about 6 per cent by weight and more specifically in an amount of about 4.8 per cent by weight.

Whenever ammonium carbonate and/or tetrasodium pyrophosphate or equivalents are present in our compositions, effective amounts up to a maximum of about 1 per cent of each builder is recommended. In all cases the amount of water is varied so as to provide a final composition totaling 100 per cent ingredients.

In compounding our inventive compositions, the order of addition of components is quite immaterial, since the desired uniform re-solution is obtained upon merely reheating a frozen solution to a liquid state, regardless of the order of compounding the ingredients. Also, the improved compositions of our invention such as the compositions which additionally contain such components as ammonium carbonate and/or tetrasodium pyrophosphates in the amounts previously presented also exhibit this desired property of complete uniform re-solution upon merely melting a frozen solution.

By way of specific examples of applicants' invention, the following compositions are given:

Example I

	Per cent by weight
Slurry mixture comprising sodium polypropylene benzene sulfonate, sodium sulfate (sulfonate to sulfate ratio=3 to 2) and 42.5% water	20.0
Sodium sulfonate obtained from SO_2 extract of petroleum (water 20%, trace sodium chloride)	4.8
Monobutyl ether of ethylene glycol	3.0
Water	72.2
	100.0

Example II

	Per cent by weight
Slurry mixture comprising sodium polypropylene benzene sulfonate, sodium sulfate (sulfonate to sulfate ratio=3 to 2) and 42.5% water	20.0
Sodium tetrahydronaphthalene sulfonate (Alkanol-S)	4.8
Monobutyl ether of ethylene glycol	3.0
Water	72.2
	100.0

Example III

	Per cent by weight
Slurry mixture comprising sodium polypropylene benzene sulfonate, sodium sulfate (ratio sulfonate to sulfate=3 to 2) and 42.5% water	20.0
Sodium tetrahydronaphthalene sulfonate (Alkanol-S)	4.8
Monobutyl ether of ethylene glycol	3.0
Ammonium carbonate	0.4
Tetrasodium pyrophosphate	0.4
Water	70.0
	100.0

Example IV

	Per cent by weight
Slurry mixture comprising sodium polypropylene benzene sulfonate and sodium sulfate (water 45.6%, sodium sulfate 21.76%, sulfonate 32.64%)	21.4
Sodium sulfonate obtained from SO_2 extract of petroleum (water 20%, trace of sodium chloride)	4.8
Monobutyl ether of ethylene glycol	3.0
Ammonium carbonate	0.4
Tetrasodium pyrophosphate	0.4
Water	70.0
	100.0

In compounding our composition, all the ingredients are charged into a suitable mechanical mixer and are agitated at 140° F. to 160° F. until homogeneous. A perfume may be added if desired after first cooling the above mixture to about 100° F., in order to mask any undesirable odor which may be present.

Samples of composition from Examples 1, 2, 3, and 4 were placed in a cold room set at about 32° F. for 24 hours. No evidence of settling out was noted in all four cases. The samples were then cooled to -6° F. In all cases the solutions were uniformly and completely frozen. Mere standing at 45° F. or higher without any agitation gave uniformly clear solutions. All four examples exhibited satisfactory foaming and detergency qualities, both before and after being frozen.

While we have presented our invention by means of illustrative examples, it is to be understood that these examples are not to be construed as limitations of our inventive contribution to the art. Rather, our invention is more accurately defined as claimed hereinafter.

We claim:

1. A concentrated detergent composition comprising an aqueous solution containing from about 7.5% to about 12.5% by weight, based on said detergent composition, of a mixture of long-chain alkali alkyl aryl sulfonate containing from 9 to 18 carbon atoms in the alkyl chain with an alkali builder therefor, and from about 1 to about 5% by weight of a water-soluble polyether alkylene selected from the group consisting of alkyl ethers of mono- and polyalkylene glycols containing less than 5 carbon atoms in the alkyl ether chain, said aqueous solution being stabilized against separation of a solid salt phase upon freezing and upon re-solution from the frozen to the melted liquid state by the addition of from about 2 to about 6% by weight of a water-soluble alkali polyalkyl benzene sulfonate derived from a liquid sulfur dioxide extract fraction of petroleum, boiling between 400°–525° F., by sulfonating said fraction and neutralizing the sulfonated product with an alkali.

2. A concentrated detergent composition as defined in claim 1, wherein said long-chain alkali alkyl aryl sulfonate is an alkali polypropylene benzene sulfonate containing from 9 to 18 carbon atoms in the polypropylene radical, and said alkali builder is an alkali sulfate.

3. A concentrated detergent composition as defined in claim 1, wherein said water-soluble polyether alkylene is monobutyl ether of ethylene glycol.

4. A concentrated detergent composition as defined in claim 1, wherein said long-chain alkali alkyl aryl sulfonate is sodium polypropylene benzene sulfonate containing from 9 to 18 carbon atoms in the polypropylene radical, said alkali builder is sodium sulfate, said polyether alkylene is monobutyl ether of ethylene glycol and said alkali polyalkyl benzene sulfonate is sodium polyalkyl benzene sulfonate.

5. A concentrated detergent composition as defined in claim 1 and further comprising up to about 1% by weight of ammonium carbonate based on said detergent composition.

6. A concentrated detergent composition as defined in claim 1 and further comprising up to about 1% by weight of tetrasodium pyrophosphate based on said detergent composition.

7. A concentrated detergent composition consisting essentially of an aqueous solution of about 21% by weight based on said detergent composition of a slurry of sodium polypropylene benzene sulfonate containing from 9 to 18 carbon atoms in the polypropylene radical, said slurry containing a mixture of said sulfonate with sodium sulfate as a builder therefor in a ratio of about 3 parts of said sulfonate to 2 parts of said sulfate, and about 45% by weight of water based on said slurry, said aqueous solution containing about 3% by weight of monobutyl ether of ethylene glycol and being stabilized by the addition of about 4.8% by weight of sodium polyalkyl benzene sulfonate derived from a liquid sulfur dioxide extract fraction of petroleum, boiling between 400 and 525° F., by sulfonating said fraction and neutralizing the sulfonated product with an alkali, and further containing sufficient additional water to make up the difference to

100% by weight of the total ingredients of the composition.

8. A detergent composition as defined in claim 7, and further containing about .4% of ammonium carbonate and about .4% of tetrasodium pyrophosphate based on the weight of said composition.

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