

UNITED STATES PATENT OFFICE

2,629,697

ALKYL ARYL SULFONATE-LIQUID HYDRO-CARBON - ALIPHATIC HYDROXY COM-POUND COMPOSITIONS

William K. Langdon and Earl F. Soop, Grosse Ile, Mich., assignors to Wyandotte Chemicals Corporation, Wyandotte, Mich., a corporation of Michigan

No Drawing. Application October 14, 1948, Serial No. 54,568

6 Claims. (Cl. 252-161)

1

This invention relates to a novel, and highly useful, liquid composition based essentially upon the ingredients: sodium alkyl aryl sulfonate, liquid hydrocarbon and an aliphatic hydroxy compound. More particularly, the sodium alkyl aryl sulfonate ingredient of our invention is sodium kerylbenzenesulfonate¹ containing not over 30% by weight Na₂SO₄; and the liquid hydrocarbon is a petroleum distillate of the kerosene type. Mixtures of sodium kerylbenzenesulfonate and a petroleum distillate hydrocarbon boiling in the kerosene range (150-300° C. at atmospheric pressure) form extremely viscous, gelled or wax-like masses which are of an opaque appearance.

However, according to our invention, when an aliphatic hydroxy compound is added to a mixture of 1 part by weight of kerosene, and 1/6-1/3 part of sodium kerylbenzenesulfonate in amounts as little as 2% by weight (all parts and percentages hereinafter given are by weight, unless otherwise stated), the mass promptly loses its viscous character, becomes very fluid and becomes transparent to translucent in appearance. The composition of our invention is therefore of value as a base product in the formulation of printing inks, paints and liquid dry cleaning compositions wherein it is sought to obtain the advantages of a surface active or wetting agent such as sodium kerylbenzenesulfonate in the presence of a liquid hydrocarbon.

Our invention also includes a single phase liquid type composition, wherein water is added to the base composition first mentioned above. We have discovered that the aliphatic hydroxy compound coupling agent renders it possible to introduce water into the composition and still maintain a clear, translucent-to-transparent, single phase liquid mass.

Such single phase, liquid mass compositions of our invention are particularly useful as emulsion type cleaning compounds for removing oil, dirt and soil from metal surfaces. The working solutions, or more accurately speaking, the working suspensions or emulsions of such single phase liquid compositions consist of approximately 1 part of liquid composition to 100 parts of water. They are also useful as base compositions in which additional detergent ingredients, such as organic solvents, water softening compounds, soil

¹ Sodium kerylbenzenesulfonate is the sodium salt of kerylbenzene sulfonic acid whose alkyl or "keryl" group is derived from a petroleum distillate fraction boiling in the range of 150-300° C. and containing 9-16 carbon atoms, corresponding to the kerosene range, hence the name "keryl"; and whose benzene group is derived from aromatic hydrocarbons of the benzene series.

2

retention agents, alkaline salts, etc. may be incorporated.

Sodium kerylbenzenesulfonate is an excellent surface active agent and detergent when employed in aqueous solutions. In the formulation of an emulsion type cleaner a lyophilic, oil-dissolving hydrocarbon, such as a petroleum distillate, is desirable. Aqueous solutions of sodium kerylbenzenesulfonate however are immiscible with such liquid hydrocarbons; even though aqueous solutions of higher alkyl aryl sulfonates, whose alkyl group contains 20-30 carbon atoms and is derived from a white oil or liquid paraffin boiling in the range of 195-295° C. at 15 mm. pressure are miscible with white oil and Stoddard solvent (cf. U. S. Patent 2,317,986). And as mentioned above, sodium kerylbenzenesulfonate and the liquid hydrocarbon form nearly solid wax-like mixtures.

We have discovered that first of all, a wax-like, opaque and highly viscous mixture of kerylbenzenesulfonate and a normally liquid petroleum distillate hydrocarbon boiling in the kerosene range can be converted to a clear, fluid mass through the medium of a coupling agent consisting of an aliphatic hydroxy compound having 4 to 10 carbon atoms and selected from the group consisting of 4 to 10 carbon atom monohydroxy aliphatic alcohols, mono(n-)butyl ether of ethylene glycol, mono(n-)butyl ether of di-ethylene glycol, mono(n-)butyl ether of propylene glycol and 2-ethylhexanediol-1,3.

Secondly, we have discovered that the foregoing resultant clear, fluid mass of sodium kerylbenzenesulfonate, petroleum distillate hydrocarbon and coupling agent is compatible with water. By the addition of critical amounts of water as hereinafter described in detail, the clear, fluid appearance of the mixture is undisturbed. Such a clear, single phase mixture can then be most readily dispersed in a relatively large volume of water, to make up the emulsion type cleaning solution or suspension, previously mentioned.

We have also discovered that the ratio of the ingredients, in order to obtain a clear, single phase mixture, must be maintained within the following stated critical ranges:

Ingredient:	Per cent by weight
Petroleum	55-71
Sodium kerylbenzenesulfonate	12-20
Water	15-25
Coupling agent	2-4

The above stated range proportions of ingredi-

ents, for convenience in formulating, can be alternatively stated as follows:

Petroleum hydrocarbon . 1 part by weight
Sodium kerylbenzenesulfonate ----- 1/6-1/3 part
Water ----- 1/4-1/2 part
Coupling agent ----- 2-4% by weight of total composition

Sodium kerylbenzenesulfonate in both its salt-free form (i. e. with Na₂SO₄ extracted) and in its salt-containing or salt-built form, can be employed in making the compositions of our invention. However we prefer to use, and find that the best results are obtained when a sodium kerylbenzenesulfonate of at least 70% active agent content (i. e. containing not over 30% of Na₂SO₄) is employed.

The following examples will serve to illustrate to those skilled in the art, and in greater detail, the manner in which the principle of our invention may be practiced.

Example 1

Sodium kerylbenzenesulfonate of the salt-free type (i. e. containing only 0.25% Na₂SO₄) in the amount of 10 grams was stirred with 30 grams of kerosene in a beaker, while warming on a hot plate. A gradual swelling of the sodium kerylbenzenesulfonate occurred, until a viscous, non-pourable, translucent wax-like mass was formed. Amyl alcohol (commercial grade of mixed amyl alcohols sold under the trade name "Pentanol"), in the amount of 1 cc. or 0.8 gram (2% by weight) was then added. After stirring for a short time, the viscosity of the mixture was substantially reduced, so that the resultant mixture was quite fluid. On adding water (approximately 15 cc.) to the mixture, a clear transparent solution was obtained. This solution formed a stable, milky emulsion when added to a large volume of water.

Example 2

Sodium kerylbenzenesulfonate containing 70% active agent (i. e. about 30% by weight Na₂SO₄) in the amount of 20 grams was mixed with 60 grams of kerosene and allowed to stand for two hours. To 60 grams of this mixture, water was added in 1 ml. increments and with vigorous agitation. After the addition of 2 ml. of water the mixture thickened and progressively became thicker until a total of 9 ml. of water had been added. The mixture was then slightly warmed, 5 more ml. of water added, followed by the addition of 1 cc. or 0.9 gram of monobutyl ether of ethylene glycol (commercial grade available

under the trade name "Butyl Cellosolve"). The viscosity of the mixture was thereby substantially decreased. Upon the addition of another cc. of monobutyl glycol ether (a total of 2.4% by weight), a less viscous and substantially clear solution or emulsion resulted.

By taking an initial formulation of the ingredients, lying within the range proportions as first hereinabove stated, and gradually increasing the amount of coupling agent (monobutyl ether of ethylene glycol) from 2 to above 4%, the critical range proportion of 2-4% thereof was established. The results are tabulated as follows:

TABLE 1

Kerosene	Water	Sodium Kerylbenzene Sulfonate (30% Na ₂ SO ₄)	Mono-butyl Ether of Ethylene Glycol	Results
55.3	24.0	18.4	2.3	Clear, fluid.
54.9	23.8	18.3	3.0	Nearly clear, fluid.
54.6	23.6	18.2	3.6	Do.
54.3	23.4	18.1	4.2	Split into 2 layers.
53.9	23.2	18.0	4.9	Do.

The foregoing 2-4% critical range content of monobutyl ether of ethylene glycol, is equally well applicable to the other selected coupling agents within the scope of our invention.

We are unable to evolve any chemical or scientific theory of why the particular aliphatic hydroxy compounds selected should be operable for the purposes of our invention. Several homologous oxy- and hydroxy-aliphatic compounds were added to a base mixture consisting of 3 grams of sodium kerylbenzenesulfonate (containing 30% Na₂SO₄), 9 grams of kerosene and 2.3 cc. of water. The addition was made in uniform 0.4 cc. amounts of the oxy- or hydroxy-aliphatic compound. Dependent upon the specific gravity of the oxy- or hydroxy-aliphatic compounds tested, this represented 2.1-2.3% by weight of the total composition. Accordingly, the test compositions conformed closely to the following formulation:

Kerosene -----	60
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄) -----	20
Water -----	18
Coupling agent -----	2

Listed in Table II below, are those particular aliphatic hydroxy compounds which were found to be operable as coupling agents, according to this test:

TABLE II

Coupling Agent	Synonym or Trade Name	Amount Added (ml.)	Appearance
Butyl Alcohol.....	n-Butanol.....	.4	Clear, fluid.
Amyl Alcohol.....	"Pentanol".....	.4	Do.
Hexyl Alcohol.....	n-Hexanol.....	.4	Do.
Octyl Alcohol.....	n-Octanol.....	.4	Do.
2-Ethyl Hexanol.....4	Do.
Decyl Alcohol.....	n-Decanol.....	.4	Translucent, fluid.
n-Butyl Ethylene Glycol Ether.....	"Butyl Cellosolve".....	.4	Clear, fluid.
n-Butyl Di-Ethylene Glycol Ether.....	"Butyl Carbitol".....	.4	Nearly clear, fluid.
2-Ethylhexanediol-1,3.....4	Transparent, fluid.
n-Butyl Propylene Glycol Ether.....4	Nearly clear, fluid.

5

On the other hand, listed below in Table III are those oxy- or hydroxy-aliphatic compounds which were not operable:

TABLE III

Coupling Agent	Synonym or Trade Name	Amount Added (ml.)	Appearance
Propyl Alcohol	iso-Propanol	.4	Clear, but split.
Tetradecyl Alcohol	n-Tetradecanol	.4	Opaque, stiff.
Mono-Ethyl Ethylene Glycol Ether	"Ethyl Cellosolve"	.4	Do.
Di-Ethyl Ethylene Glycol Ether	"Di-Ethyl Cellosolve"	.4	Do.
Mono-Methyl Di-Ethylene Glycol Ether	"Methyl Carbitol"	.4	Do.
Diacetone	Diacetone Alcohol	.4	Opaque, slightly stiff.
Dimethyl Dioxane	Di-Propylene Oxide	.4	Clear, stiff.
Pentanediol-1,5	Amylene Glycol	.4	Opaque, stiff.
Triethanolamine		.4	Do.

The critical range proportions of ingredients as first hereinbefore stated, are further substantiated and illustrated by the following test results. A base formulation was made up as follows:

	Percent
Kerosene	72.4
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄)	12.0
Water	15.6

Varying amounts of coupling agent were then added to this base formulation so that the resultant test range formulation was substantially as follows:

	Percent
Kerosene	71
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄)	12
Water	15
Coupling agent	1.7-2.2

The results are shown in Table IV:

TABLE IV

Coupling Agent	Amount Present, Percent by Weight	Results
Amyl Alcohol ("Pentanol")	1.71	Split into 2 layers.
Do.	2.08	Nearly clear, fluid.
2-Ethyl Hexanol	1.38	Nearly clear and stiff, but split on standing.
Do.	2.16	Clear, fluid.

As further examples of formulations embodying the principle of our invention, and those which are particularly well suited for commercial purposes as a base mixture for the making up of emulsion type cleaning solutions, we specify the following:

Example 3

	Percent
Kerosene	63
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄)	20
Water	15
Monobutyl ether of ethylene glycol ("Butyl Cellosolve")	2

Example 4

	Percent
Kerosene	60
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄)	20
Water	18
2-ethylhexanediol-1,3	2

Example 5

	Percent
Kerosene	55
Sodium kerylbenzenesulfonate (30% Na ₂ SO ₄)	24
Water	18
Amyl alcohol ("Pentanol")	3

6

The formulation of Example 5 was found to be particularly excellent in that it was capable of being subjected to extremely low temperature

conditions (i. e., frozen with solid carbon dioxide), such as might be encountered under certain storage conditions, and on being restored to the liquid state by warming to room temperature, retained its single phase character.

Equivalent modes of practicing our invention may be followed provided that they are within the scope and purview of the appended claims.

We, therefore, distinctly claim and particularly point out as our invention:

1. A single phase, non-viscous, fluid composition consisting essentially of 55-71% by weight of a normally liquid petroleum distillate hydrocarbon boiling in the kerosene range, 12-20% of a sodium kerylbenzenesulfonate of not over 30% Na₂SO₄ content and whose keryl group contains 9-16 carbon atoms; 15-25% water; and 2-4% of an aliphatic hydroxy compound selected from the group consisting of 4 to 10 carbon atom monohydroxy aliphatic alcohols, monobutyl ether of ethylene glycol, monobutyl ether of diethylene glycol, monobutyl ether of propylene glycol and 2-ethylhexanediol-1,3.

2. A single phase, non-viscous, liquid composition suitable for use as a base product for the make-up of oil-in-water and water-in-oil type emulsions, consisting essentially of a petroleum distillate liquid hydrocarbon boiling in the kerosene range, 1/6-1/3 part by weight of sodium kerylbenzenesulfonate per part of liquid hydrocarbon; said sodium kerylbenzenesulfonate having not over 30% Na₂SO₄ content and a keryl group containing 9-16 carbon atoms; 1/4-1/2 part of water per part of liquid hydrocarbon; and 2-4% by weight, total composition basis, of an aliphatic hydroxy compound selected from the group consisting of 4 to 10 carbon atom monohydroxy aliphatic alcohols, monobutyl ether of ethylene glycol, monobutyl ether of diethylene glycol, monobutyl ether of propylene glycol and 2-ethylhexanediol-1,3.

3. An emulsion forming composition consisting essentially of 55-71% by weight of kerosene, 12-20% of sodium kerylbenzenesulfonate of not over 30% Na₂SO₄ content and whose keryl group contains 9-16 carbon atoms, 15-25% of water and 2-4% of an aliphatic hydroxy compound selected from the group consisting of 4 to 10 carbon atom monohydroxy aliphatic alcohols, monobutyl ether of ethylene glycol, monobutyl ether of diethylene glycol, monobutyl ether of propylene glycol and 2-ethylhexanediol-1,3.

4. A clear, single phase liquid composition consisting of approximately 63% by weight of kerosene, 20% of sodium kerylbenzenesulfonate of not over 30% Na₂SO₄ content and whose keryl group contains 9-16 carbon atoms, 15% of water and 2% of monobutyl ether of ethylene glycol.

5. A clear, single phase liquid composition consisting of approximately 60% by weight of kerosene, 20% of sodium kerylbenzenesulfonate of not over 30% Na_2SO_4 content and whose keryl group contains 9-16 carbon atoms, 18% of water and 2% of 2-ethylhexanediol-1,3. 5

6. A clear, single phase liquid composition consisting of approximately 55% by weight of kerosene, 24% of sodium kerylbenzenesulfonate of not over 30% Na_2SO_4 content and whose keryl group contains 9-16 carbon atoms, 18% of water and 3% of amyl alcohol. 10

WILLIAM K. LANGDON.
EARL F. SOOP.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,228,407	Schuler	Jan. 14, 1941
2,317,986	Flett	May 4, 1943
2,356,205	Blair	Aug. 22, 1944
2,409,671	Faust	Oct. 22, 1946
2,469,378	Flett	May 10, 1949
2,531,166	Shaw	Nov. 21, 1950