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DRY CLEANING SOLVENT CONTAINING HALOALKYLDIPHENYL OXIDE SULFONATES

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The present invention relates to new detergents and their use in dry cleaning compositions and more particularly refers to a substantially water-insoluble dry cleaning fluid containing an alkali metal salt of an alkylated halogenated diaryl oxide sulfonate.

The dry cleaning industry employs a variety of water-insoluble solvents for cleaning soiled fabrics. These include perchloroethylene, trichloroethylene, carbon tetrachloride, Stoddard solvent, etc. It is common practice to add to these dry cleaning fluids various surface-active agents to remove water-soluble stains from the materials being cleaned. In the early days of detergent use it was found that the addition of some water to the solvent mixture was necessary in order for the detergent to function properly and for water-soluble soils such as salt, sugars and perspiration to be removed. Any water-soluble salt or stain not removed during dry cleaning treatment was later removed by a time-consuming and expensive method known as "spotting." It was also found that the addition of too much water would cause shrinkage and wrinkling or have other detrimental effects upon the fabric. Since that time the dry cleaning industry has had the problem of finding means and solvent compositions which would maintain the water concentration in the solvent within the limits required for efficiency of the detergent without adverse effects upon the fabric.

It is therefore an object of this invention to provide improved dry cleaning detergents and compositions. A further object is to provide a dry cleaning composition which provides an adequate control of the effective water concentration in the solvent. Other objects and advantages will become apparent during the course of the following description.

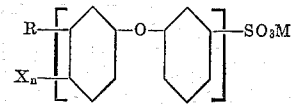
It has been discovered that if an alkali metal salt of an alkylated halogenated diaryl oxide sulfonate is added to substantially water-insoluble dry cleaning fluid, a solvent composition is produced which shows outstanding and unusual properties, both as concerns cleaning effectiveness and as concerns control of effective water concentration in the solvent. In the commercial dry cleaning practice it was found that the relative vapor pressure of water (P/P_0 where P and P_0 are, respectively, the partial pressure of water vapor in equilibrium with the composition and with pure water) in the dry cleaning solvent containing a soap or detergent was an important factor in determining the acceptability of the solvent and this value became known as "solvent relative humidity." A study of this problem is to be found in ASTM Bulletin for September of 1953 on pages 65–68 (TP 153 et seq.). It was established that if the solvent relative humidity was less than 0.65 the soap or detergent would not function properly in the removal of water-soluble soils and stains in the material. If the solvent relative humidity was greater than 0.80 the fabric would be subject to wrinkling or shrinkage due to the presence of excessive water. A range of from about 0.70 to 0.75 is the preferred range. As soiled materials are added to the dry cleaning system, the water content, and consequently the solvent relative humidity, of the system increases because of the water carried by the fabric.

The rate of increase of solvent relative humidity with increasing water content is dependent upon the particular

soap or detergent employed with the solvent and upon its concentration. It is obviously desirable that a solvent-detergent composition be employed wherein the rate of increase of solvent relative humidity with increasing water concentration be as low as possible. The solvent relative humidity for a system containing any given amount of soap or detergent, however, cannot be predicted in advance by any method currently known.

It is surprising, therefore, to find that the use of an alkylated halogenated diaryl oxide sulfonate salt with any of the known dry cleaning solvents produces a solvent-detergent mixture with an ability to allow the addition of greatly increased quantities of water and still remain within the desired solvent relative humidity range. In addition to this advantage, a combination of dry cleaning solvent with a haloalkylaryl oxide sulfonate salt shows an improved ability to remove water-soluble soils. To the dry cleaning industry this means a reduction of spotting and a greatly simplified dry cleaning procedure. The dry cleaning solvent, in order to obtain a dry cleaning composition having the highly desirable characteristics, should contain about 0.25 to 20 percent, and preferably about 3 to 6 percent, by weight, of the alkylated halogenated diaryl oxide sulfonate salt.

Alkylated halogenated diaryl oxide sulfonate salt as used herein is defined by the formula



wherein R represents an aliphatic hydrocarbon radical having from 8 to 22 carbon atoms inclusive, M represents an alkali metal, X represents a halogen having an atomic number of from 17 to 35 inclusive and *n* is an integer from 1 to 2. In the above formula, any of the substituent groups outside the brackets may be attached independently to either of the aromatic nuclei.

The following examples are illustrative of the practice of the invention but are not to be considered as limiting its scope.

EXAMPLES 1–6

In order to obtain solvent relative humidity values for the compositions of this invention and to have a standard method for comparison of these values with those obtainable with known solvent detergent systems, standard ASTM equipment and procedures were employed. The steps of this procedure and equipment employed are described in more detail in ASTM Bulletin (PB 153) for September 1953 on pages 64–67. The procedure followed was to place 500 cc. of dry cleaning solvent containing 20 grams of the detergent to be tested into a 1000 cc. flask. The flask was placed in a constant-temperature oven at 80 degrees F. and stirred with a hollow impeller connected to a hollow shaft. As the impeller was rotated, air was forced through the solvent, past a humidity-sensing element which was connected to a recorder and back through the hollow shaft and impeller into the solvent. The stirring was continued until the recorder indicated that equilibrium had been reached. At this time about 0.5 gram of water was added to the system and stirring was continued until equilibrium was again reached. This process was continued until a solvent relative humidity of about 90 had been obtained. The results of several such experiments are shown in the table below, wherein the relative humidity of the solvents at various water contents is shown. From these data it is evident that the detergents of the present invention tolerate a much higher water content in the dry cleaning fluid without exceeding the desirable humidity range than do the detergents currently used in the industry.

Water tolerance of dry cleaning compositions

Ex. No.	Solvent	Detergent	Relative Humidity, Percent, as a Function of Water Content								
			0.1 H_2O	0.2 H_2O	0.3 H_2O	0.4 H_2O	0.5 H_2O	0.6 H_2O	0.7 H_2O	0.8 H_2O	0.9 H_2O
1	C_2Cl_4	Petroleum Sulfonate [a]	66	75	84						
2	C_2Cl_4	Fatty Amine Condensate [a]	57	66	72	80	82				
3	C_2Cl_4	Octyldichlorodiphenyl Oxide SO_3Na	55	63	69		78				
4	C_2Cl_4	Pentadecyldichlorodiphenyl Oxide SO_3Na	58			71		79	88		
5	C_2Cl_4	4-Dodecyl-4'-Chlorodiphenyl Oxide SO_3Na	32	48	58	65	73	75	79	88	
6	Varsol [b]	Pentadecyldichlorodiphenyl Oxide SO_3Na	44	51	55	59	63	66	70	74	79

[a] Commercial detergents widely used in the dry cleaning industry.
[b] Commercial solvent widely used in the dry cleaning industry.

Similar results were obtained with other standard dry cleaning solvents, such as Stoddard's solvent.

EXAMPLE 7

This experiment was made to demonstrate the effectiveness of the compounds of this invention in the removal of water-soluble soils from fabric in the presence of water-insoluble solvents. A strip of rayon crepe 4" wide and 30' long was passed through a 1.5 N NaCl solution, through a wringer, past a bank of infrared lamps and finally wound onto a pickup reel. 4 x 4" swatches were then cut from the strip for testing. Every twentieth swatch was analyzed for salt content by a standard method of extracting with water and analyzing the water for chloride ion. A test solution was prepared by placing 64 grams of detergent in sufficient organic solvent to make a total volume of 1600 ml. Sufficient water was then added to produce a solvent relative humidity of 75%. 400 ml. of this solution was placed in each of the four beakers of a Terg-O-Tometer. Two weighed swatches were then placed in each beaker and the Terg-O-Tometer was operated for thirty minutes at 75 cycles per minute and 75 degrees F. At the end of this period the swatches were removed, drained and air-dried by hanging on a line. When dry, the swatches were analyzed for salt content and percent salt removed was calculated therefrom. The following results were obtained:

Dry cleaning detergent:	Percent salt removal in perchloroethylene
Dodecylchlorodiphenyl oxide sodium sulfonate	27.8
Fatty amine condensate	20.3
Petroleum sulfonate	13.5
Blank	4.7

Similar results are obtained in actual dry cleaning of soiled clothing and by use of other alkylhalodiphenyl oxide sulfonates of this invention.

Some of the chlorinated alkylated diphenyl oxide sulfonates used in the present invention and methods for their production are described in the copending application of two of us (Valenta and Steinhauer) entitled "Alkylated Chlorinated Diaryl Oxide Sulfonic Acids and Their Salts," Serial No. 735,681, filed May 16, 1958, now abandoned. The others may be made by the same general methods with appropriate obvious modifications in the materials and procedures used. Thus, the dihalo compounds may be prepared by condensing (1) dihalophenol with bromobenzene, (2) halophenol with chlorobromobenzene or dibromobenzene, (3) phenol with dichlorobromobenzene or tribromobenzene or by (4) halogenating diphenyl oxide until the dihalo stage is reached and then (5) alkylating, sulfonating and neutralizing the product as described in the cited copending application. Such a synthesis is illustrated by the following example.

EXAMPLE 8

1. PREPARATION OF DICHLORODIPHENYL OXIDE

Chlorine was sparged into diphenyl oxide containing 1% by weight of ferric chloride, the temperature being maintained at about 40° C., until the increase in weight corresponded to the dichloro ether. The product was then degassed, washed, dried and distilled.

2. ALKYLATION OF DICHLORODIPHENYL OXIDE

To 359 g. of dichlorodiphenyl oxide containing 13.85 g. of anhydrous aluminum chloride there was added dropwise with stirring 126 g. of tripropylene, the temperature being maintained at 60–63° C. Stirring was continued for one hour after the addition was complete, after which the reaction mixture was cooled, washed with water and distilled at 160–210° C. at 0.8 mm. pressure.

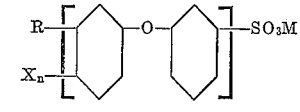
3. SULFONATION OF ALKYLDICHLORODIPHENYL OXIDE

One tenth mole (48.5 g.) of nonyldichlorodiphenyl oxide was dissolved in 200 ml. of methylene chloride. The solution was maintained at 9–17° C. while a solution of 10.4 g. of sulfur trioxide in 75 ml. of methylene chloride was slowly added with stirring. Fifteen minutes after the addition was complete, 350 ml. of water was added with stirring and the mixture was then neutralized with 50% aqueous sodium hydroxide. The water was then evaporated from the mixture, thus leaving a solid which was then ground to a tan powder. It was readily soluble in water and ethanol.

Various homologs of the above product were prepared by substantially the same procedure.

We claim:

1. A substantially water insoluble dry cleaning solvent having dissolved therein from about 0.25 to 20 percent by weight of a salt of an alkylated halogenated diaryl oxide sulfonate having the formula



wherein R is an aliphatic hydrocarbon radical having from 8 to 22 carbon atoms, inclusive, M is an alkali metal, X is a halogen having an atomic number of from 17 to 35 inclusive and n is an integer from 1 to 2.

2. A dry cleaning solvent composition as defined in claim 1 wherein the solvent is perchloroethylene.

3. A dry cleaning solvent composition as defined in claim 1 wherein the solvent is Stoddard's solvent.

4. A dry cleaning solvent composition as defined in claim 1 wherein the alkali metal is sodium.

5. A dry cleaning solvent composition as defined in claim 1 wherein the halogen is chlorine.

6. A dry cleaning solvent composition as defined in claim 1 wherein the number of halogen atoms, n, is 2.

7. A dry cleaning solvent composition as defined in claim 1 wherein the salt is dodecylchlorodiphenyl oxide sodium sulfonate.

8. A dry cleaning solvent composition as defined in claim 1 wherein the salt is octyldichlorodiphenyl oxide sodium sulfonate.

9. A dry cleaning solvent composition as defined in

claim 1 wherein the salt is pentadecyldichlorodiphenyl oxide sodium sulfonate.

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