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2,828,326

SULFOPHTHALATE ESTERS

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No Drawing. Application February 3, 1956
Serial No. 563,186

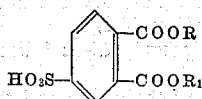
7 Claims. (Cl. 260—470)

The present invention is directed to certain branched-chain hexyl and heptyl esters of 4-sulfophthalic acid and their salts.

The alkali, amine and ammonium salts of these esters are valuable as surface active agents, particularly as wetting agents.

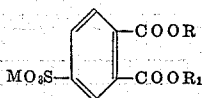
Some esters of sulfophthalic acid are known surface active agents. The sulfophthalates are useful in some applications where other surface active agents cannot be used; for example, the sulfo-group is more resistant to hydrolysis than the sulfate group, and sulfophthalates can be used in some textile treating applications in which the heat or caustic would hydrolyze alkyl sulfates. Moreover, the sulfophthalates are less expensive than some similar surface active agents, e. g., the sulfobenzoates.

The new compounds of our invention are the sulfophthalates of the following formula, and the salts thereof:



where each of R and R₁ are selected from the group consisting of 2-methylpentyl, 2,4-dimethylpentyl, and 2-methylhexyl.

Our novel sulfophthalates and their salts can both be represented by the formula:



in which R and R₁ have the same meaning as above, and M is hydrogen or a salt-forming cation.

It has now been discovered that our branched alkyl 4-sulfophthalate salts, e. g., the salts of di-(2-methylpentyl) 4-sulfophthalate, di-(2,4-dimethylpentyl) 4-sulfophthalate, and di-(2-methylhexyl) 4-sulfophthalate have greatly superior wetting activity compared to that of straight chain alkyl 4-sulfophthalate salts, and also have a wetting activity greater than that of di-(2-ethylbutyl) 4-sulfophthalate salts.

All of our sulfophthalate esters are characterized by a 2-methylpentyl group and 6 to 7 carbon atoms; i. e., the 2-methylpentyl, 2,4-dimethylpentyl, and 2-methylhexyl (2,5-dimethylpentyl)sulfophthalates can all be considered as 2-methylpentyl sulfophthalates.

Another desirable property of our novel 2-methylpentyl 4-sulfophthalates is their high degree of solubility in water which makes them useful in some applications where less soluble wetting agents cannot be used.

Another factor which makes our particular sulfophthalate esters preferable to sulfophthalate esters of straight chain alcohols, is the fact that our branched-chain alcohols are readily prepared by a Guerbet condensation, while some straight chain alcohols, e. g., n-hexanol, must be prepared by more expensive procedures.

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The branched chain alcohols can also be prepared by an Oxo process.

While ordinarily our esters are produced by diesterification with a single alcohol, a mixture of the alcohols can be used to produce a mixed ester, and the salts of these mixed esters also have valuable wetting activity. For example, the following mixed esters can be produced: 2-methylpentyl 2-methylhexyl 4-sulfophthalate, 2-methylpentyl 2,4-dimethylpentyl 4-sulfophthalate, and 2-methylhexyl 2,4-dimethylpentyl 4-sulfophthalate. Mixtures of these mixed esters can be produced, and mixtures can be made from di-esters produced by esterification with a single alcohol, or mixtures can be made from mixed esters and esters of single alcohols, and all of the mixtures of esters and individual esters of the present invention form salts of good wetting activity.

The invention is illustrated by the examples below.

EXAMPLE 1

To a 500 ml. flask fitted with a stirrer, thermometer and drying tube, 127.5 grams (1.25 moles) of 2-methylpentanol-1 was charged. 4-sulfophthalic anhydride, 132 grams (0.544 mole based on assay of 93.7%), was melted and poured at 70 to 80° C. into the alcohol during a period of 10 minutes. The reaction flask was cooled by a water bath so that the temperature did not exceed 55° C. The reaction mixture was then heated rapidly to 90° C. and stirred at 90–95° C. for 15 minutes. The solution was allowed to cool and was slowly poured into dilute sodium hydroxide solution so that the pH was maintained slightly alkaline. Approximately 300 ml. of ethyl alcohol was added to make the total volume of solution about 1 liter, and the solution was filtered and then drum-dried at atmospheric pressure and 50–55 lbs. steam pressure to obtain 176.4 grams of the sodium salt of di-(2-methylpentyl) 4-sulfophthalate.

The 2-methylpentanol-1 used in the above procedure was obtained by a Guerbet condensation of n-propanol. In this condensation n-propanol, 600 grams, was heated in a bomb with 20 grams of fine copper powder, 30 grams of calcium oxide, and 32 grams of tripotassium phosphate to about 260° C. under an autogenous pressure of 900–1000 pounds per square inch for 20 hours. The 2-methylpentanol-1 was distilled in 96.3% yield at 147–149° C., n_D^{25} 1.4165, d_4^{20} 0.826.

EXAMPLE 2

Using the procedure of Example 1, 42.9 grams of 4-sulfophthalic anhydride (93.8% assay) was heated with 45 grams of 2,4-dimethylpentanol-1. The reaction mixture was cooled and was slowly poured into an alcoholic aqueous solution of sodium hydroxide and the final pH was adjusted to 7.5–8.0. The solution was filtered and diluted to about 800 ml. with ethanol and water. The solution was drum dried at 55–60 lbs. steam pressure to obtain the sodium salt of di-(2,4-dimethylpentyl) 4-sulfophthalate as a fine powder.

The 2,4-dimethylpentanol-1 used in the present procedure was obtained by a Guerbet condensation of approximately equimolar amounts of n-propanol and isobutanol, using a powdered copper catalyst and a temperature of 275° C. for 20 hours, in the presence of small amounts of potassium phosphate and calcium oxide. The dimethylpentanol had a boiling point of 156 to 160° C.

EXAMPLE 3

Using the procedure of Example 2, 47.9 grams of 4-sulfo-ortho-phthalic acid was esterified with 50.2 grams of 2-methylhexanol-1. Only 63.2 grams of di-(2-methylhexyl) 4-sulfophthalate salt were produced, but losses were heavy during drying as the product was a fine dust.

The 2-methylhexanol-1 used in the above procedure

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was prepared by a Guerbet condensation of 4 moles of n-butanol with 6 moles of n-propanol in a bomb at 260° C. for 20 hours. The alcohol had a boiling point, 162–167° C., and a refractive index of $n_D^{25.5}$ 1.4211.

The particular novel sulfophthalates of the present invention have unusually high wetting activity. The table below compares the wetting activity of the compounds of Examples 1 to 3 with the wetting activity of the sodium salt of di-(2-ethylbutyl) 4-sulfophthalate. The values recorded in the table are the wetting times in seconds as determined by the Draves-Clarkson test (American Dye-stuff Reporter, vol. 28, pages 420–428, Aug. 7, 1939). This test measures the time required for a weighted, standardized skein of cotton yarn to sink in a stated concentration of the wetting agent in aqueous solution.

Table I

Esterifying Alcohol	Wetting Time (Seconds)		
	0.25%	0.125%	0.0625%
2-methylpentanol-1.....	3.4	7.3	48.7
2-methylhexanol-1.....	4.4	9.2	39.8
2,4-dimethylpentanol-1.....	4.1	8.6	34.0
2-ethylbutanol-1.....	4.8	12.7	75.4

Table I demonstrates that the 2-methylpentanol esters of the present invention are markedly superior in wetting activity to the 2-ethylbutyl ester. The esters of the present invention are also superior in wetting activity to any of the other known soluble sulfophthalate ester salts.

The compounds of our invention also have a remarkable foaming activity, and a great ability to stabilize foams, as shown by the Ross-Miles test recorded in Table II below in which the centimeters of foam formed were measured at once, and after five minutes.

Table II

Sodium sulfophthalate Ester (0.1% Concentration)	Centimeters of Lather			
	Soft Water (50 p. p. m.)		Hard Water (300 p. p. m.)	
	At Once	After 5 Min.	At Once	After 5 Min.
2-methylpentyl.....	9.9	8.7	11.3	10.5
2-methylhexyl.....	17.6	17.6	9.3	9.0
2,4-dimethylpentyl.....	13.2	13.2	9.9	9.6

The very slight to no loss in foam height after standing 5 minutes is particularly notable, and demonstrates good foam stabilizing ability. This property makes our

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compounds useful in the preparation and stabilization of aerosol foams for shaving, shampooing, etc.

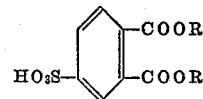
The salts of our novel ester compounds are formed by neutralizing our esters so that one valence of the sulfo group is satisfied by an alkali metal, an alkaline earth metal, an organic amine, or an ammonium ion. Representative cations which can be used are Na^+ , Ca^+OH , NH_4^+ , K^+ , etc.; in fact, any of the salts obtained by neutralizing the sulfo group with the following bases are useful: ammonia, ethanolamine, diethanolamine, triethanolamine, alkylamines such as ethylamine, t-butylamine and t-octylamine, morpholine, lime, calcium carbonate, magnesium carbonate, potassium hydroxide, etc., and in general all water solubilizing cations.

Novel (2-methylpentyl), (2-methylhexyl), and (2,4-dimethylpentyl) 4-sulfophthalate compounds and their salts have been prepared and described, and have been demonstrated to be particularly valuable wetting agents.

The present invention provides soluble alkyl sulfophthalate type wetting agents which are markedly superior to those known to the art.

We claim:

1. As new compounds, sulfophthalates of the following formula, and the salts thereof:



in which R is selected from the group consisting of 2-methylpentyl, 2,4-dimethylpentyl, and 2-methylhexyl radicals.

2. As a new compound, di-(2-methylpentyl) 4-sulfophthalate.

3. As a new compound, the sodium salt of di-(2-methylpentyl) 4-sulfophthalate.

4. As a new compound, di-(2,4-dimethylpentyl) 4-sulfophthalate.

5. The sodium salt of the compound of claim 4.

6. As a new compound, di-(2-methylhexyl) 4-sulfophthalate.

7. The sodium salt of di-(2-methylhexyl) 4-sulfophthalate.

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