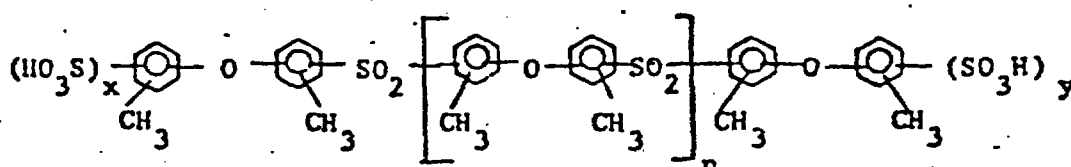


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SULPHONIC ACID SUBSTITUTED DI-TOLYLETHER SULPHONES
USEFUL AS DISPERSING AGENTS

The present invention relates to sulphonic acids of ditolyloether sulphones, their production and use as dyeing assistants.

More particularly, the present invention provides sulphonic acids of ditolyloether sulphones of formula I,



in which n is 0 to 6,

each of x and y , independently, is 0 or 1 with

the proviso that $x + y$ is at least one, or salts thereof.

Preferred compounds of formula I are those which are derived from an isomeric mixture of ditolyloethers, especially those obtained as a byproduct in the preparation of cresols.

The compounds of formula I are useful as levelling agents when dyeing substrates dyeable with anionic dyestuffs or with disperse dyestuffs.

Further, the compounds of formula I are useful as dispersing agents for disperse dyes and as dispersing agents or emulsifying agents for pesticides, herbicides and other agrochemicals and as tanning assistants in the tanning of leather.

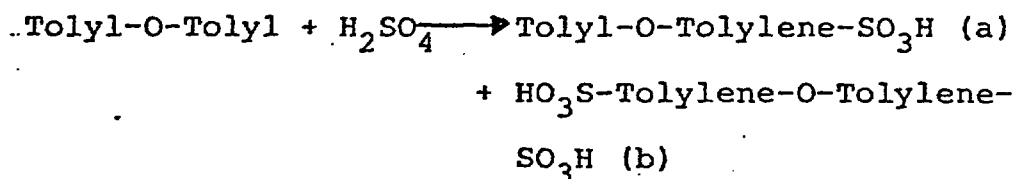
For these uses the compounds of formula I are advantageously in salt form. Suitable salt forms of the compounds of formula I include alkali metal, alkali earth metal and ammonium salts, such as sodium, lithium, magnesium, calcium, ammonium, mono-, di- and triethanol-ammonium and mixtures thereof.

The compounds of formula I may be prepared in analogy with known methods, for example in analogy with the methods described in Swiss Patent 470,367. Basically, sulphonation is effected with 1 to 1.6 mols conc. sulphuric acid per mol tolylether at 110°C and with vacuum distillation of the water of reaction, condensed at 190° until the reaction product is water soluble and has a constant acid value. It will be appreciated that the reaction product is a mixture of compounds of different grades of sulphonation. The reaction can be illustrated as follows:

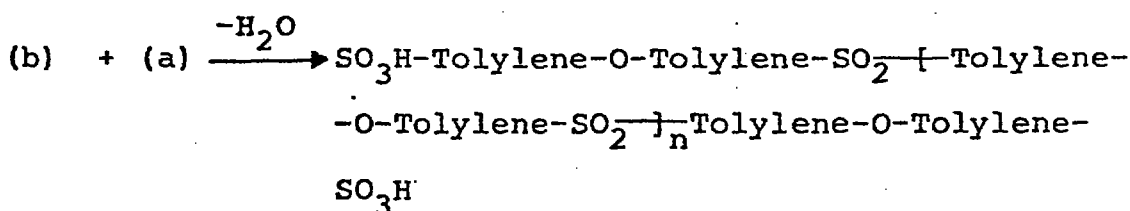
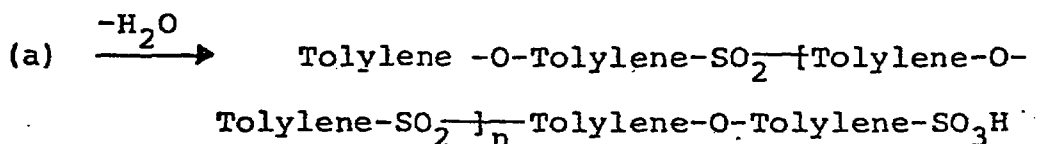
- 1) Sulphonation at temperature of up to 110°C

(11)

- 3 -



2) Condensation at temperature up to 190°C (in vacuo)



The acid value of the end product is between 300 and 390 m val/100g.

The compounds of formula I may be employed in the form of aqueous preparations or in solid form. After production the compounds of formula I need not be isolated and can be used after diluting or spray drying.

The present invention further provides a dyeing assistant composition comprising (i) a compound of formula I or a salt thereof in admixture with (ii) the condensation product of castor oil with 20 to 50 mols ethylene oxide. Suitably the ratio of (i) to (ii) is from 1:8 to 8:1, preferably from 1:2 to 2:1. This composition can also contain up to 50% by weight based on (ii) of a condensate of a fatty acid e.g. oleic acid with 5 to 10 mols ethylene oxide. This composition is particularly suitable as a levelling agent for

dyeing polyamide and/or polyester fibres, especially by high temperature process.

The compounds of formula I may be employed as levelling agent either before dyeing, during dyeing or after dyeing. The pre-treatment is suitably effected at temperatures of from 20 to 100°C, preferably 50 to 100°C in a weakly acid medium. The after treatment is suitably effected at 60 to 140°C, preferably from 80 to 130°C.

Dyeing and printing in the presence of compounds of formula I as levelling agents may be carried out in accordance with known methods for dyeing or printing substrates with anionic dyestuffs or disperse dyestuff. The amount of compound of formula I employed in the pre- or post-treatment bath or in the dyebath will depend on the textile substrate, the dyestuffs employed, the pH of the bath and the treatment time. In general suitable amounts are in the range of from 0.02 to 20% by weight, preferably 0.1 to 15% by weight based on the weight of the substrate.

The preferred substrates are polyesters, cellulose acetate and natural or synthetic polyamides.

The compounds of formula I have anti-foaming properties and result in level dyeings especially in the case of stripy nylon. The other properties of the dyed substrate such as light-fastness are not

(13)

- 5 -

deteriously affected but rather improved.

When the compounds of formula I are employed as dispersing agents they are employed in accordance with known methods and in conventional amounts.

When the compound of formula I is employed as a tanning assistant it is suitably employed in amounts of from 5 to 20% by weight based on the tanning agent (solids), preferably about 10% by weight.

The compounds of formula I can also be reacted with from 0.2 to 3 mols formaldehyde, a formaldehyde yielding agent or methylol compound/mol compound of formula I in the presence of strong sulphuric acid (pH below 1). The products are also useful as dispersing agents for disperse dyestuffs.

The following Examples further serve to illustrate the invention. In the Examples all parts are by weight and all temperatures in degrees Centigrade.

Example 1

588 Parts sulphuric acid (98%) are added under nitrogen atmosphere with vigorous stirring and cooling to 792 parts ditolyether over a period of 30 to 45 minutes. After addition the temperature is between 100 and 105°. The reaction is continued for 5 $\frac{1}{2}$ to 6 hours. The mixture is heated to 120° in 10 to 20 minutes under a vacuum (10-15 torr). After 20 to 30 minutes the water of the reaction is practically fully removed. Reducing the vacuum to 3 to 6 torr the reaction mixture is heated for approximately 15 minutes to a temperature between 160 and 180° and the whole is kept at this temperature for about 6 hours until the acid resin produced has an acid content of 330 to 390 m val/100 g. The reaction mixture is cooled (without vacuum) in 10 to 15 minutes, to 125 to 130°. The product, without isolation, is then further treated with 500 parts demineralised water which is at a temperature of 8-12°. (The nitrogen atmosphere can be removed). The aqueous solution of the resin is cooled to 90 to 100° and 355 parts of aqueous ammonia (25%) are added slowly thereto over a period of 30 minutes with cooling. After the addition the temperature of the solution is 30 to 35°. Stirring is effected for about 30 minutes at 20-30° until a fully homogeneous solution is obtained. The weak viscous solution has a

(19)

- 7 -

pH in the range of 6.5 to 7. The solution may then be diluted with 270 parts water and stored used as such or it can be converted to a powder by spray drying.

Example 2

A 50% aqueous solution of the product of Example 1 (50% active material) in the ammonium salt form is mixed with 16% by weight based on the active material. of condensate of castor oil with 32 mols ethylene oxide. The viscous solution is stable on storage.

Example 3

40 Parts anhydrous product of Example 1 (in acid free form) are stirred with 60 parts condensate of castor oil with 32 mols ethylene oxide at 100° until homogeneity is obtained. Subsequently 12 parts monoethanolamine are added with cooling. When 50 parts are added a viscous storage-stable product is obtained.

Example 4

A similar product to that of Example 3 is obtained by mixing 10, 90, 3 and 15 parts of the given ingredients in place of the 40, 60, 12 and 50 parts , respectively.

Example 5

15 Parts anhydrous product of Example 1 are neutralized with 5 parts monoethanolamine. 12 parts paraffin oil, 4 parts condensate of oleic acid with 6 mol

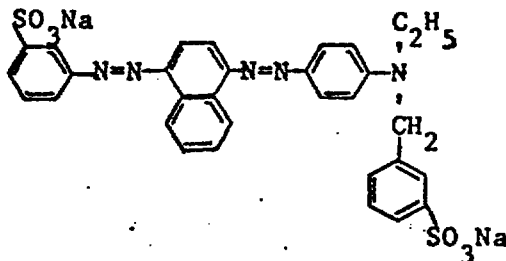
ethylene oxide, 60 parts condensate of castor oil with 32 parts ethylene oxide and 4 parts water are added and stirred until homogeneity is obtained. The product is especially suitable as a levelling agent for the high temperature dyeing of polyester.

Example 6

10 Parts anhydrous product of Example 1 and 47 parts ethanol are neutralized with 3 parts monoethanolamine. Then 40 parts of carrier consisting basically of trimethylbenzenes as described in DOS 2 033 894 in the Table under 3, column 6 are added and the whole is stirred until homogenous. A clear yellow solution with good levelling properties for dyeing polyester by the high temperature process is obtained. Similar results are obtained employing instead of 40 parts trimethylbenzene, 40 parts ditolyether.

Example 7

100 Parts stripey nylon are dyed in a dyebath (liquor to goods ratio 40:1) containing 0.35 parts dye of formula



3 parts NaH_2PO_4 and 6 parts compound of Example 1 (100% active ingredients-ammonium salt). The bath pH

is 6 and the fabric is put into the bath at 50° whereupon the bath is heated to 98-100° in 45 minutes and dyeing is carried out at this temperature for 60 minutes. The substrate is then rinsed and dried. A level, stripe-free red brown dyeing is obtained.

Example 8

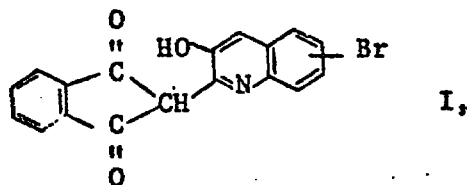
A yarn consisting of 50 parts nylon 6.6 and 50 parts Spandex fibres (Lycra, Trade Mark, Dupont) are dyed in a bath (liquor to goods ratio 40:1) containing 0.25 parts sodium salt of 1-amino-2-bromo-4-(4'-methylphenylamino)-anthraquinone-2'-sulphonate, 2 parts acetic acid and 2 parts of the ammonium salt of the compound of Example 1 (100% active substance). The yarn is added to the bath at 35° and the bath is heated to 95° in 40 minutes. Dyeing is effected for 1 hour at this temperature. Both yarns is equally dyed in the same tone of blue. With 4 parts of the composition of Example 2 equally good results are obtained.

Example 9

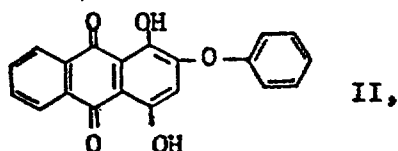
A bobbin of polyester texturised yarn is dyed at a liquor to goods ratio of 10:1 in a bath at 130° containing demineralised water (pH 4.5 adjusted with acetic acid) 1 g/l compound of Example 1 in the NH_4 salt form (100% active material) and 1 g/l of the condensate of castor oil with 30 mols ethylene oxide

18

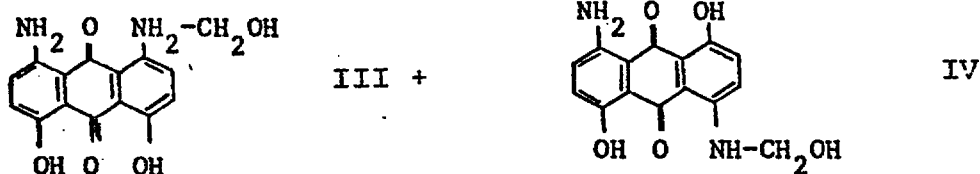
0.46% dyestuff of formula I



0.52% dyestuff of formula II



0.17% dyestuff mixture of equally quantities of dyes of formulae III and IV



The amount of liquid flowing was equivalent of 20 l/kg per minute. After 30 minutes treatment at 130° the whole is cooled, the bath is run off and the substrate is subjected to reductive clearance. Equally good results are obtained employing 2 g/l of the composition of Example 2.

19

- 11 -

Example 10

A polyester fabric (Dacron, Trade Mark) is dyed with 0.25 g/l Foron Rubin SE-GFD (Trade Mark) with the addition of 2 g/l ammonium sulphate and 2 g/l compound of Example 1 (NH_4 salt 100% active substance) at pH 5. The liquor to goods ratio is 20:1. The dyeing is begun at 20° and the bath is heated to 70° in 10 minutes. The dyeing is completed after 20 minutes at 130°. A level dyeing is obtained. Using the same amount of the compounds of Examples 2 to 5 equally good results are obtained.

Example 11

214 Parts of C.I. Disperse Blue 73 (pure dyestuff) in the form of a presscake are stirred well with 1050 parts of solution of the compound of Example 1 (389 parts active substance for 16 hours until a lump-free suspension is obtained. The suspension is put through a sieve then homogenised for 2 hours in a homogenising machine until the majority of the particles are 1 μ or less. The homogenate is spray-dried and 603 parts of a dyestuff powder having good dispersion stability are obtained. The dyestuff powder also gives good dye yield on textile substrates.

Example 12

A storage stable 60% tanning liquid is made from
8 parts $\text{Cr}(\text{SO}_4)_3$ (powder)
4 parts ammonium salt of Example 1 (100% active

20

ingredients).

0.5 parts formic acid and

7.5 parts water.

Using this tanning liquid, leather of good quality is obtained employing the chrome-tanning process.

[Zirconium sulphate in place of chromium sulphate gives equally good results].

Example 13

80 Parts herbicide N-(3,4-dichlorophenyl)-N'-N'-dimethyl urea is ground with 5 parts compound of Example 1 (NH₄ salt 100% active material) 1.25 parts dibutyl naphthalenesulphonate 4 parts silica gel and 9.5 parts alumina.

In a 1% dispersion in water having 5° German Hardness less than 25% of the agent is precipitated.

Example 14

3 Parts C.I. Disperse Blue 71 powder are stirred to homogeneity with 10 parts of a 30% aqueous solution of the compound of formula I, then ground in a mill having glass beads of 0.4 to 0.6 mm for 50 minutes. The suspension obtained has good storability and is easy to use.

Example 15

To 680 Parts ditolyether (isomeric mixture of di-methyldiphenylether) are added dropwise under

(21)

- 13 -

nitrogen atmosphere, 588 parts (concentration 98%) sulphuric acid over 40 minutes at 108°.

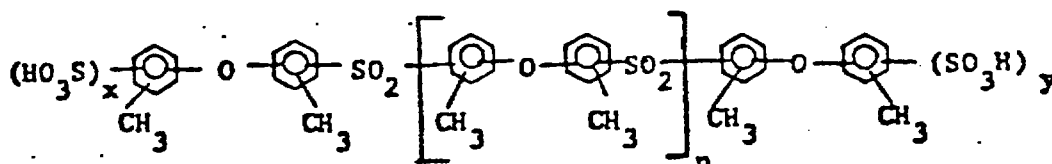
After stirring the reaction mixture for 6 hours at 100° the temperature is raised to 120° under vacuum (15 torr). Condensation is effected at this temperature for 1 hour. Subsequently the whole is heated to 160° under increased vacuum (0.1 to 1.1 torr). After a further 6 hours at 160°, 1051 parts of a sulphone with an acid value of 381 m val/100 g is obtained. 86.8 parts sulphone and 20 parts water are warmed to 100°. After the solution is homogeneous, 6.3 parts formaldehyde (35.8%) and 2 parts (vol.) sulphuric acid (concentration 98%) are added. Condensation is effected for 14 hours at 102°. The viscous brown solution obtained is neutralized with ammonium hydroxide and dried on a rotary evaporator or in vacuo. The product is a light brown powder which is easily soluble in water. Neutralization with an equivalent amount of $\text{NH}_4\text{OH}/\text{Mg}(\text{OH})_2$ yields, after spray drying, a light grey-brown powder which is well soluble in water.



22

CLAIMS

1. A compound of formula I,



in which n is 0 to 6,

each of x and y, independently, is 0 or 1 with

the proviso that x + y is at least one,

or salts thereof.

2. A process for the production of a compound of formula I as stated in Claim 1, comprising sulphonating a tolylether with 1-1.6 mols concentrated sulphuric acid per mol tolylether and subsequently condensing the sulphonated tolylether .

3. A process according to Claim 2, in which condensation is carried out at temperatures of up to 190°C.

4. A process for the production of a compound of formula I according to Claim 2 in which an isomeric mixture of tolylethers is employed.

5. A process for the production of a compound of formula I, or a salt thereof, as defined in Claim 1, substantially as hereinbefore described with reference to Example 1.

6. A compound of formula I, or a salt thereof,

23



- 15 -

whenever obtained by a process according to any one of Claims 2 to 5.

7. A process for the production of a disperse dyestuff preparation comprising grinding a disperse dye in the presence of a compound of formula I.

8. A process for the production of a disperse dyestuff preparation substantially as hereinbefore described with reference to Example 9.

9. A disperse dyestuff preparation whenever obtained by a process according to Claim 7 or Claim 8.

10. A process for dyeing or printing substrates dyeable with anionic dyestuffs or substrates dyeable with disperse dyestuffs comprising employing a compound of formula I, as levelling agent either before, during or after dyeing.

11. A process according to Claim 10, in which the amount of compound of formula I is from 0.02 to 20% by weight of the substrate.

12. A process according to Claim 10 or Claim 11 in which the substrate consists of or comprises cellulose acetate, polyester or natural or synthetic polyamides.

13. A process according to any one of Claims 10 to 12, in which the compound of formula I is admixed with the condensate of castor oil and 20 to 50 mols ethylene oxide.



24

- 16 -

14. A process for dyeing or printing substrates dyeable with anionic or disperse dyestuffs, substantially as hereinbefore described with reference to any one of Examples 7 to 11.

15. A dyed or printed substrate whenever obtained by a process according to any one of Claims 10 to 14.

16. A dyeing assistant composition comprising (i) a compound of formula I as defined in Claim 1 or Claim 6, in admixture with (ii) the condensate of castor oil with 20 to 50 mol ethylene oxide.

17. A composition according to Claim 16, in which the ratio of (i) to (ii) is from 1:8 to 8:1.

18. A composition according to Claim 17, in which the ratio of (i) to (ii) is from 1:2 to 2:1.

19. A composition substantially as hereinbefore defined with reference to any one of Examples 1 to 6.

20. A process for the production of tanned leather comprising employing a compound according to Claim 1 or Claim 6, as tanning assistant.

21. A process for the production of tanned leather substantially as hereinbefore described with reference to Example 12.

22. Tanned leather whenever obtained by a process according to Claim 20 or Claim 21.



23. A process for the preparation of dispersions or emulsions of herbicides or pesticides comprising employing a compound according to Claim 1 or Claim 6 as dispersant or emulsifier.

24. A process according to Claim 23, substantially as hereinbefore described with reference to Example 13.

25. The condensate of a compound of formula I as defined in Claim 1 or Claim 6, with 0.2 to 3 mols formaldehyde, formaldehyde yielding agent or methylol compound / mol of compound of formula I.

26. A condensate according to Claim 25, substantially as hereinbefore defined with reference to Example 15.

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