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WATER-SOLUBLE MOTHPROOFING AGENT

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The present invention relates to water-soluble moth-proofing agents.

Hitherto water-soluble moth-proofing agents have been manufactured by introducing sulfo or carboxylic acid groups into the aromatic nucleus of compounds being effective but insoluble in water and having phenolic hydroxy groups. Another way was by using for the synthesis such starting materials as contain sulfo or carboxylic acid groups in an aromatic nucleus. Water-soluble moth-proofing agents of this kind, however, have the disadvantage that they are less effective when compared with the corresponding compounds bearing no sulfo or carboxylic acid groups, as by the introduction of such groups for rendering the moth-proofing agents water-soluble, their effectiveness is more or less diminished.

In accordance with the present invention it has been found that the aromatic sulfocarboxylic acid esters of water-insoluble moth-proofing agents, which contain at least one free phenolic hydroxy group, represent valuable water-soluble moth-proofing agents. Obviously the same applies to the corresponding water-soluble salts of the aromatic sulfocarboxylic acid esters as, for instance, the alkali metal salts. Therefore, the appended claims are intended to cover the free acid esters as well as their water-soluble salts. The great advantage of the aromatic sulfocarboxylic acid esters consists in that the effectiveness is not diminished by the presence of the acid ester group. On the contrary in some cases the effectiveness is increased, whereas, when sulfonic or carboxylic acid groups are directly introduced into moth-proofing agents containing phenolic hydroxy groups, the effectiveness is more or less diminished. The new aromatic sulfocarboxylic acid esters are distinguished by an excellent levelling capacity. They can be employed for rendering goods liable to the attack of moths with the same effectiveness from an acid as well as from a neutral bath. They are, therefore, especially suited for the treatment of mixed tissues consisting of wool and artificial silk, which in many cases are advantageously treated in a neutral bath. By this property they are superior to known moth-proofing agents, for instance those described in the U. S. Patent 1,707,181, which only in an acid bath show a sufficient affinity to the vegetable fiber.

The process for obtaining the new aromatic sulfocarboxylic acid esters consists in acting with monohalides or anhydrides of aromatic sulfocarboxylic acids in the presence of a tertiary base upon moth-proofing agents being insoluble in water, but containing at least one free phenolic hydroxy group. The reaction may be performed, for instance, as follows:

The calculated amount of the carboxylic acid sulfo chloride is dissolved at elevated temperature in anhydrous pyridine, and in portions the calculated amount of the phenol is added. The reaction is finished after a treatment of one or two hours. The phenolic hydroxy groups are totally or partially esterified, that is—as it may be supposed—with the carboxylic acid group. As starting materials there come into consideration all kinds of water-insoluble moth-proofing agents containing at least one free phenolic hydroxy group as, for instance, naphthols, compounds derived from diphenyl, diphenylmethane, triphenylmethane, as for example:

1-methyl-3,6-dibromo-β-naphthol,
1,3,6-tribromo-2-naphthol,
2,4-dibromo-1-naphthol,
1-chloro-6-bromo-2-naphthol,
Dibromo-1-chloro-2-naphthol,
6-bromo-1-methyl-2-naphthol,
2,2' - dihydroxy-3,3',5,5'-tetrachloro-dihydroxy-diphenyl,
2,2'-dihydroxy - 3,3',5,5' - tetrabromo-dihydroxy-diphenyl,
4,4'-dihydroxy-3,3'-dichloro-diphenyl,
2,2' - dihydroxy-3,3'-tetramethyl-diamido - 5,5'-dichloro-diphenyl-methane,
2,2'-dihydroxy-5,5'-dichloro-diphenyl-methane,
2,2' - dihydroxy-3,3'-dimethyl-5,5'-dichloro-diphenyl-methane,
2,2' - dihydroxy-4,4'-dichloro-diphenyl-methane,
2,2' - dihydroxy-3,3' - dimethyl-4,4'-dichloro-diphenyl-methane,
2,2'-dihydroxy-4,4'-dimethyl - 5,5' - dichloro-diphenyl-methane,
2,2' - dihydroxy - 3,3',5,5' - tetrachloro-diphenyl-methane,
2,2',5,5'-tetrachloro-4,4' - dihydroxy - diphenyl-methane,
2,2'-dihydroxy-3,3',5,5',6,6' - hexachloro - diphenyl-methane,
2,2'-dihydroxy-5,5'-dichloro - triphenyl-methane,
2,2'-dihydroxy - 5,5',2'' - trichloro - triphenyl-methane,
2,2'-dihydroxy-3,3'-trimethyl-5,5',2'' - trichloro-triphenyl-methane,
2,2' - dihydroxy - 5,5',4'' - trichloro-triphenyl-methane,
2,2'-dihydroxy - 3,3',5,5',2'',6'' - hexachloro-triphenyl-methane,

2,2'-dihydroxy-3,3',5,5',2'',4'' - hexachloro - triphenyl-methane,
2,2' - dihydroxy - 3,3',5,5',3'',4'' - hexachloro-triphenyl-methane,
2,2' - dihydroxy-3,3' - dimethyl - 5,5',2'',4'',5'' - pentachloro-triphenyl-methane,
2-hydroxy-3,5,3',5'-tetrachloro-2',2''-sulfone-triphenyl-methane,
2,2',3'' - trihydroxy - 3,3',5,5',2'',4'',6'' - heptachloro-triphenyl-methane,
3,2'-dihydroxy-2,4,6,3',5'-pentachloro - 4''-nitro-triphenyl-methane,
2-hydroxy - 3,5,3',5',4'' - pentachloro-2',2''-sulfone-triphenyl-methane,
3,2'-dihydroxy-2,4,6,3',5' - pentachloro-3''-nitro-triphenyl-methane,
2,2' - dihydroxy - 3,3',5,5',4'' - pentachloro-triphenyl-methane,
2,2' - dihydroxy - 3,3',5,5',2'' - pentachloro-triphenyl-methane,
2,2'-dihydroxy - 3,3',5,5',2'' - pentachloro-6''-fluoro-triphenyl-methane,
2,2' - dihydroxy - 3,3',5,5'-tetrachloro-2'',6''-difluoro-triphenyl-methane,
2,2' - dihydroxy-3,3',5,5',2'',4'',5'' - heptachloro-triphenyl-methane.

As sulfocarboxylic acids, the halides of which, their anhydrides respectively, may be employed, may be mentioned, for instance, sulfobenzoic acid, sulfosalicyclic acid, sulfophthalic acid, diphenylcarboxylic acid, aliphatic sulfocarboxylic acids as well as their substitution products.

My new compounds may be employed in the usual manner in aqueous solution at an elevated temperature and, if desired, in the presence of acids, as stated above.

The following examples illustrate the invention without, however, restricting it thereto, the parts being by weight:

Example 1

45 parts of benzoic acid sulfochloride (2 mols) are dissolved in nearly 100 parts of anhydrous pyridine at 70–80°, then 33.8 parts of 2,2'-dihydroxy-3,3',5,5'- tetrachloro-diphenyl-methane (1 mol) are subsequently added with stirring. The mixture is cooled after a treatment of about one hour. For working up the reaction product is diluted with water and the ester, its sodium salt respectively, is separated with sodium chloride after acidifying the solution.

Example 2

By causing to react 2 mols of salicyclic acid sulfochloride with 1 mol of 2,2'-dihydroxy-3,3',5,5',4''-pentachlorotriphenylmethane in the presence of pyridine according to Example 5, the disulfocarboxylic acid ester of the above compound is obtained in form of a colorless powder.

Example 3

By causing to react 2 mols of benzoic acid-p-sulfochloride with 1 mol of 2,2'-dihydroxy-3,3',5,5',4''- pentachlorotriphenylmethane-2'',6'-sulfone in the presence of pydirine according to Example 5, the disulfocarboxylic acid ester of the above compound is obtained in form of a colorless powder.

Example 4

54 parts of the sulfochloride of the naphthalene-2-carboxylic acid are dissolved in 120 parts of anhydrous pyridine, and to this solution 52 parts of 2,2'-dihydroxy-3,3',5,5',2'',4'',5''-heptachlorotriphenylmethane are subsequently added with stirring. After a treatment of one hour and a half a weakly colored, clear reaction mixture is obtained, from which the ester, its sodium salt respectively, is obtained by salting out with sodium chloride after having acidified the mixture.

Example 5

46 parts of benzoic acid-m-sulfochloride are dissolved in 100 parts of anhydrous pyridine at a temperature of about 80°, and to this solution 52 parts of 2,2'-dihydroxy-3,3',5,5',2'',4'',5''-heptachlorotriphenylmethane are subsequently added with stirring. The reaction is finished after a stirring of one to two hours. On diluting with water and acidifying the ester, its sodium salt respectively, separates by salting out with sodium chloride.

By treating woolen tissue for instance with 1% of the ester thus obtained (calculated on the weight of the material to be proofed) according to the dyeing process with the addition of acetic acid and sulfuric acid for one hour at boiling temperature, the tisssue is really protected to the attack of moths.

The same protective effect is obtained by treating mixed fabrics, consisting of wool and viscose stable fiber, with 1% (calculated on the weight of the material to be proofed) of the above compound in a neutral bath with the addition of 10% of Glauber's salt for one hour at a temperature of 95°.

The other substances may be employed in a similar manner.

I claim:

1. Water-soluble moth-proofing agents consisting of aromatic sulfocarboxylic acid esters of aromatic hydroxy compounds containing halogen atoms selected from the group consisting of hydroxynaphthalenes, hydroxydiphenyls, hydroxydiphenylmethanes and hydroxytriphenylmethanes.

2. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of aromatic hydroxy compounds containing halogen atoms selected from the group consisting of hydroxynaphthalenes, hydroxydiphenyls, hydroxydiphenylmethanes and hydroxytriphenylmethanes.

3. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of hydroxydiphenylmethanes containing halogen atoms.

4. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of hydroxytriphenylmenthanes containing halogen atoms.

5. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of hydroxytriphenylmethanes containing at least four halogen atoms.

6. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of hydroxytriphenylmethanes containing at least four chlorine atoms.

7. Water-soluble moth-proofing agents consisting of benzene sulfocarboxylic acid esters of dihydroxydiphenylmethanes containing halogen atoms.

8. A water-soluble moth-proofing agent consisting of the benzene sulfocarboxylic acid ester of 2,2'-dihydroxy-3,3',5,5',2'',4'',5''-heptachlorotriphenylmethane.

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