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2,867,658

HALO SUBSTITUTED SULFANILIDES

Wilhelm E. Frick, Birsfelden, Switzerland, assignor to J. R. Geigy A.-G., Basel, Switzerland, a Swiss firm

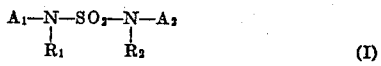
No Drawing. Application May 6, 1957 Serial No. 657,016

Claims priority, application Switzerland May 18, 1956

6 Claims. (Cl. 260—551)

The present invention is concerned with insecticidal agents, the use thereof for the protection of keratin material from injury by insects and, finally the material protected with the help of these agents.

It has been found that sulphamides of the general Formula I



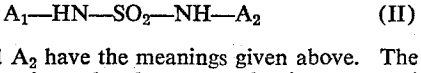
(I)

wherein:

R_1 and R_2 represent hydrogen or low alkyl radicals and A_1 and A_2 represent benzene radicals, possibly nonionogenically further substituted, which contain in all at least four halogen atoms,

have very good insecticidal activity. This is chiefly effective against insects which injure keratin fibres such as moths, fur and carpet beetles, so that these compounds are valuable auxiliary agents, in particular in the textile industry.

The sulphamide derivatives usable according to the present invention are new. They can be produced by methods known per se from known starting materials. A simple process consists in condensing, possibly in steps, suitably substituted amines with sulphuryl chloride. The condensation is performed advantageously in the presence of hydrochloric acid binding agents. Sulphamide can also be used instead of sulphuryl chloride and in this case, the condensation can be performed both in indifferent solvents or diluents as well as, possibly, in the melt. By condensing two different amines with sulphuryl chloride advantageously in two steps, unsymmetrically substituted sulphamides are obtained. A further method of production consists in alkylating halogenated N.N'-diphenyl sulphamides of the general Formula II



(II)

wherein A_1 and A_2 have the meanings given above. The alkylation is performed advantageously in aqueous/alkaline solution at a moderately raised temperature with sulphuric acid alkyl esters; naturally it can also be performed with alkyl halides. Finally, the new compounds can be produced by halogenating N.N'-diphenyl sulphamides.

In the compounds usable according to the present invention, in particular the methyl, ethyl, propyl and butyl radicals are meant by alkyl groups and, for technical and economical reasons, chiefly chlorine is meant by halogen. Apart from halogen atoms and trifluoromethyl groups, the phenyl radicals can contain other, advantageously non-ionogenic, substituents such as, e. g. alkyl, alkoxy and aryl ether groups, nitro and cyano groups. Those compounds are particularly active insecticides in which the phenyl radicals are trichlorinated. Very particularly valuable compounds are the symmetrically formed compounds, in particular the N.N'-di-(trichlorophenyl)-sulphamides and the N.N'-dimethyl and N.N'-diethyl derivatives thereof.

The following are examples of amines of the benzene series corresponding to the formula A—NH_2 which are used as starting materials: 2.4-, 3.5- or 3.4-dichloro- or dibromo - 1 - aminobenzene, 2.4.5- or 3.4.5 - trichloro - 1-aminobenzene, 3-chloro-4-bromo-1-aminobenzene, 3-trifluoromethyl-1-aminobenzene, 3-trifluoromethyl-4-chloro-1 - aminobenzene, 3,4 - dichloro - 6 - methyl - 1 - aminobenzene and 4 - trifluoromethyl - 2.5 - dichloro - 1-aminobenzene.

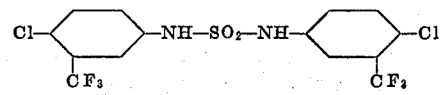
The sulphamide compounds usable according to the present invention are colourless to weakly yellowish coloured powders or viscous liquids. They dissolve in the usual organic solvents. Insofar as they can form salts, i. e. when R_1 or R_2 represents hydrogen, the alkali salts are easily formed and are soluble in water. They are applied to keratin material from organic solution or from aqueous solution or suspension.

They can be applied from dyebaths, chiefly together with the so-called "neutral to weakly acid-drawing" dyestuffs. A particularly favourable property of the sulphamide derivatives according to the present invention is that they draw on to keratin fibres even from relatively low temperatures (30 to 60°) and are fast to washing and rubbing. This is a very valuable property as it enables the application to be made under conditions which protect the fibres. The application however, is not limited to the use of aqueous solutions or suspensions. Also organic solutions of the active substances, e. g. in aliphatic or aromatic, possibly chlorinated, hydrocarbons which are used for dry cleaning of clothes, can be used to fix the agents on the keratin material. Finally, the active substances can also be used in the form of dispersions or powders, possibly blended with carriers.

The following examples serve to illustrate the invention without limiting it in any way. In these examples parts are given as parts by weight and the temperatures are in degrees centigrade. The relationship of parts by weight to parts by volume is as that of kilogrammes to litres.

Example 1

0.4 g. of the monosodium salt of a compound of the formula:



are dissolved in 500 ccm. of water. 10 g. of wool are treated in this solution for 30 minutes at about 40°. After rinsing, the wool is dried in the usual way and tested as to moth-proofness according to SNV (Swiss Association for Standardisation) Normenblatt 95 901. It is found to be mothproof.

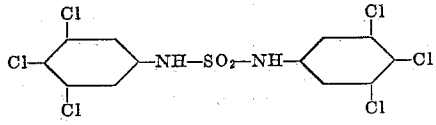
The active substance used in this example can be produced, for example, in the following way:

391 parts of 3-trifluoromethyl-4-chloraniline are dissolved in 500 parts of abs. pyridine and the solution is cooled to −5°. 134 parts of sulfuryl chloride are slowly added dropwise while stirring well so that the temperature does not exceed 0°. After the dropwise addition of sulphuryl chloride, the reaction mixture is heated to room temperature and then allowed to stand for about 20 hours at this temperature. It is then diluted with chloroform and the pyridine is removed in the usual way by shaking out with diluted hydrochloric acid. The residue is washed with water and the chloroform is evaporated off. The evaporation residue is a crystalline mass which melts at 110–115°. Recrystallised from benzene, N.N'-bis-(3 - trifluoromethyl-4-chlorophenyl)-sulphamide melts at 117–118.5°.

The compound dissolves easily in diluted caustic soda

lye and in most organic solvents except petroleum ether.

A similar result is obtained if, in the above example, instead of 0.4 g. of N.N'-bis-(3-trifluoromethyl-4-chlorophenyl)-sulphamide, 1.0 g. of a compound of the formula:



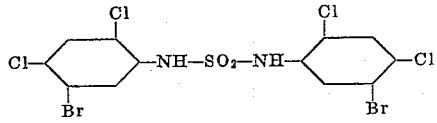
is used.

Example 2

0.1 g. of N.N'-bis-(2.4.5-trichlorophenyl)-sulphamide (melting point 158–160°) in the form of the monosodium salt is dissolved in 2 litres of water and 50 g. of wool are treated for 30 minutes in this solution at 90°. After rinsing and drying, on testing according to the SNV (Swiss Association for Standardisation) Normenblatt 95 901, the wool proves to be resistant to attack by moth larvae.

The compound used in this example can be produced in a manner analogous to that described in Example 1 from 2.4.5-trichloraniline and sulphuryl chloride.

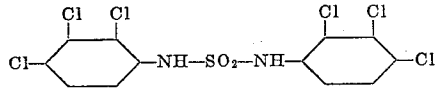
An analogous result is obtained if, in this example, instead of N.N'-bis-(2.4.5-trichlorophenyl)-sulphamide, 0.4 g. of N.N'-bis-(2.4-dichloro-5-bromophenyl)-sulphamide of the formula:



is used.

Example 3

The compound of the formula:



N.N'-bis-(2.3.4-trichlorophenyl)-sulphamide, is dissolved in a 10% concentration in ethanol. 1 part of this solution is diluted with 10 parts of a dry cleaning agent (e. g. white spirit) and the wool which is to be impregnated is treated with this solution. The material is then squeezed out to 100% of its weight and dried in the usual way.

After testing according to the SNV (Swiss Association for Standardisation) Normenblatt 95 901 the wool is found to be moth proof.

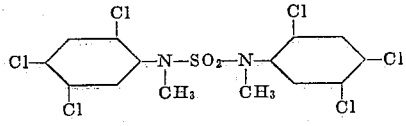
The active substance used in this example can be produced analogously to the N.N'-bis-(3-trifluoromethyl-4-chlorophenyl)-sulphamide used in Example 1.

The pure compound melts at 146–148°.

A similar result is attained if in this example, instead of a 10% solution of N.N'-bis-(2.3.4-trichlorophenyl)-sulphamide in alcohol, a 30% solution of N.N'-bis-(3.4-dichlorophenyl)-sulphamide in methyl Cellosolve is used.

Example 4

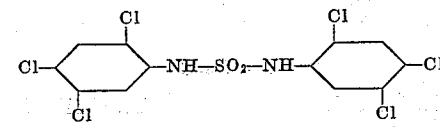
0.75 part of a compound of the formula:



is dissolved in 20 parts of alcohol and the solution is poured into a solution of 2 parts of sulphonated formyl castor oil in 5000 parts of water. The resulting suspension can be used for moth-proofing 100 parts of wool. The wool is treated by circulating it well for 1 hour at boiling temperature. It is then rinsed and dried. On testing the wool with larvae of *Tineola biselliella*, it was found to be proof to attack by these insects. The test was made according to the SNV (Swiss Association for Standardisation) Normenblatt 95 901.

The compound used in this example can be produced in the following manner:

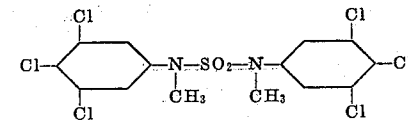
45.5 parts of a compound of the formula:



are dissolved at about 50° in 1200 parts of 2 N-caustic soda lye. 25 parts of dimethyl sulphate are added dropwise at this temperature. The solution is kept continually alkaline by the gradual addition of caustic soda lye.

After cooling, the precipitate which is to some extent oily, is taken up in ether, the ethereal solution is washed with caustic soda lye and water, dried with sodium sulphate and concentrated. The residue is recrystallised from ligroin when it then has a melting point of 153–154°.

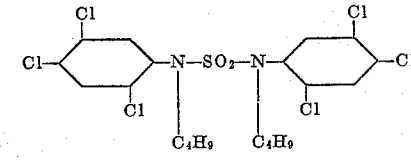
If in the above example, instead of the N.N'-dimethyl-N.N'-di-(2.4.5-trichlorophenyl)-sulphamide, 1.2 parts of a compound of the formula:



are used, then moth-proofed wool is also obtained. This compound can be produced in a completely analogous manner. It melts at 123–125°.

Example 5

10 parts of wool flannel are soaked in a solution of 20 parts of a compound of the formula:

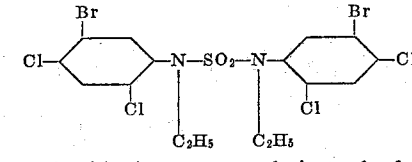


in 1000 parts of a dry cleaning agent. This solution is produced by dissolving the compound in 20 parts of alcohol and then diluting to 1 litre with white spirit. The soaked wool is squeezed out to about 100% of its weight and dried in the usual way.

On testing according to the SNV (Swiss Association for Standardisation) Normenblatt 95 901, the wool proves to be sufficiently moth-proof.

The active substance used in this example is obtained in the usual way by alkylating N.N'-di-(2.4.5-trichlorophenyl)-sulphamide with butyl bromide in benzene.

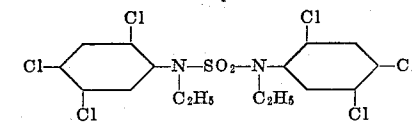
A compound of the formula:



can be used with the same result instead of that used in the above example. It can be produced in an analogous manner.

1.2 parts of the compound of the formula:

Example 6

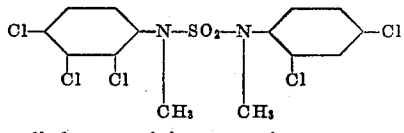


are dissolved in 20 parts of methyl Cellosolve and the solution is diluted while stirring with a solution of 2.5 parts of sulphite waste liquor in 5000 parts of water. 50 parts of wool are treated in this liquor for 30 minutes at 60°. The wool is rinsed and dried in the usual way.

The material is moth-proof tested by the method given in Example 4. It proves to be resistant to attack by pests which are injurious to keratin material.

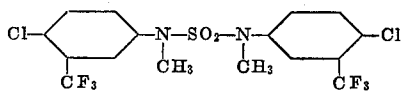
The compound used in this example is obtained by the method given in Example 4, the alkylating of the hexachlorodiphenyl sulphamide being performed with diethyl sulphate instead of with dimethyl sulphate. The pure compound melts at 78–79°.

A compound of the formula:



can be applied to wool in an analogous manner. This compound melts at 155–156°. Applied in an amount of 1.5 parts according to the above example, it has a good moth-proofing effect.

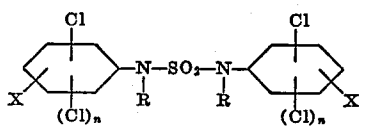
A compound of the formula:



which can be produced by methylating N.N'-di-(4-chloro-3-trifluoromethylphenyl)-sulphamide, can be used with the same success.

What I claim is:

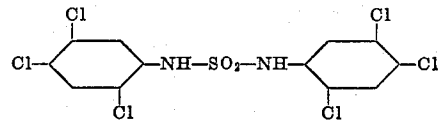
1. An insecticidal compound of the formula:



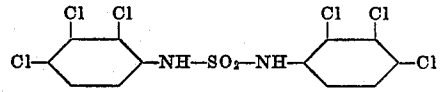
wherein R represents a member selected from the group consisting of hydrogen and lower alkyl radicals, X repre-

sents a member selected from the group consisting of Cl, Br and CF_3, and n is one of the numerals 0 and 1.

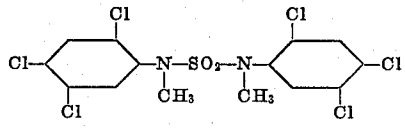
2. The insecticidal compound of the formula:



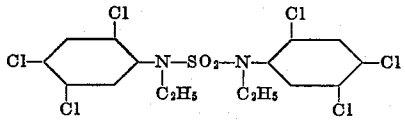
3. The insecticidal compound of the formula:



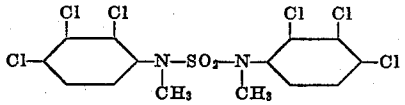
4. The insecticidal compound of the formula:



5. The insecticidal compound of the formula:



6. The insecticidal compound of the formula:



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