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2,774,708

ALKYL DIMETHYL DICHLOROBENZYL AMMONIUM MERCAPTOBENZOTHAZOLATES AND PESTICIDAL CONCENTRATES CONTAINING THE SAME

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6 Claims. (Cl. 167—33)

The present invention relates to new and valuable alkyl dimethyl dichlorobenzyl ammonium 2-mercaptobenzothiazolates which are useful as pesticides in a non-aqueous solvent.

It is known to react a quaternary ammonium compound with a chlorine substituted mercaptobenzothiazole to produce a water-insoluble compound known as cetyl dimethylbenzyl ammonium 2-(5-chlorobenzothiazyl)-sulfide and to apply the same to textile fabrics to render them proof against mildew or other fungus attack. We have found, however, that such a compound so applied is not as satisfactory or effective as our compounds and that it is not possible to apply the same to a textile fabric in such a manner as to obtain good durability of resistance against mildew or other fungus attack. The compound is applied by dissolving it in acetone and by dipping the textile material in such solution or in a suspension to which water has been added, or the solution or a suspension may be sprayed on the textile material. This has been found to produce only a transitory germicidal effect which is not as durable as the antiseptic activity of our compound, and the use of a special chlorine substituted mercaptobenzothiazole makes the treatment relatively expensive.

It is, therefore, an object of the present invention to produce a new derivative of alkyl dimethyl benzyl ammonium mercaptobenzothiazolate wherein the benzyl group of the quaternary ammonium moiety is dichloro substituted in the benzene ring and wherein the mercaptobenzothiazole moiety is unsubstituted.

Another object of the invention resides in the production of alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate and the preparation of a pesticidal concentrate therefrom in a non-aqueous solvent as a new product of commerce.

Our invention is predicated upon the discovery that alkyl dimethyl 3,4-dichlorobenzyl 2-mercaptobenzothiazolate is an unusually and exceptionally active and effective material as a pesticide, fungicide and bactericide, and that the substitution of two chlorine atoms in the benzene ring of the benzyl group produces great advantages which are unexpected and surprising.

The data presented in this table indicates that the 3,4-dichlorobenzyl derivative of this compound is about 3-5 times more effective as a germicide and protectant than the unsubstituted chemical. This significant superiority is novel and unexpected.

We have found, moreover, that the two substituent chlorine atoms may also be in the 2,4 positions of the benzene ring of the benzyl group but that, so far as we are presently aware, one of the substituent chlorine atoms must be in the 4-position in the benzene ring.

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TABLE 1

Comparison of the influence of the dichloro-substitution in the benzyl group of alkyl dimethyl benzyl ammonium 2-mercaptobenzothiazolate upon biological activity

Type of Test	Benzyl Derivative	3,4-dichlorobenzyl Derivatives	Ratio of Effectiveness
	Concentration in p. p. m. for complete inhibition		
1. Mycelial inhibition <i>Aspergillus niger</i> (chemical in nutrient agar).....	1,000	200	1:5
2. Bacteriostasis, <i>Aerobacter aerogenes</i> (chemical in synthetic liquid media).....	100	20	1:5
	Concentration, p. p. m.		
3. Inhibition of Spore Germination, <i>Macrosporium sarcinaeforme</i> : LD ₈₄	10.0	2.8	1:3.6
LD ₅₀	5.2	1.2	1:4.3
	Percent Seedling Emergence		
4. Seed Protection against Soilborne Organisms: A. Peas dipped in 5% aqueous dispersion.....	*68	*82	1:1.2
B. Corn dipped in 5% aqueous dispersion— Test I.....	9	35	1:3.9
Test II.....	20	78	1:3.9

*Least significant difference at 1:19 odds=8.9%. Least significant difference at 1:99 odds=12.9%.

TABLE 2

Comparison of bactericidal activity of alkyl dimethyl 3,4-dichlorobenzyl ammonium chloride and alkyl dimethyl 2,4-dichlorobenzyl ammonium chloride against *Salmonella typhosa* using the phenol coefficient technique

	Maximum Killing Concentration in 10 Minutes but not in 5 Minutes
3, 4-dichlorobenzyl derivative.....	1:47,000
2, 4-dichlorobenzyl derivative.....	1:40,000

Conclusion.—The 2,4-derivative is 15% less effective.

The preferred and best compound in accordance with the present invention is alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate. This may be produced by reacting alkyl dimethyl 3,4-dichlorobenzyl ammonium chloride with sodium 2-mercaptobenzothiazolate, the reaction being effected in aqueous solution at room temperature and requiring no special reaction conditions to be observed. When an aqueous 2-mercaptobenzothiazolate solution is added to the alkyl dimethyl 3,4-dichlorobenzyl ammonium chloride in aqueous solution a precipitate immediately forms which is a somewhat waxy light colored solid having a melting point of 116–118° C. after recrystallization from an ethanol-water or dimethyl formamide-water mixture. The alkyl dimethyl 3,4-dichlorobenzyl ammonium chloride may be produced in known manner from alkyl dimethyl benzyl ammonium chloride (benzalkonium chloride) and the particular

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mode of dichlorination of this well-known quaternary ammonium compound does not per se form a part of or a limitation upon this invention.

In a modified form of the invention, the corresponding 2,4-dichlorobenzyl compound is similarly produced and has similar properties, which are, however, not quite as good as those of the 3,4-dichlorobenzyl compound which

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benzyl compound and the 2,4-dichlorobenzyl compound but may contain either one alone and preferably contains the 3,4-dichlorobenzyl compound alone which has been found to have such superior properties. The treated textile fabrics are highly resistant to leaching and can be washed or dry-cleaned, if necessary, without serious loss of treating compound.

TABLE 3

Durability of mildew-resistance activity of cotton and duck containing alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate. Test method of Federal Stock Catalog CCC-T-191a using Chaetomium globosum in sterilized agar-plate method

Treatment	Chemical concentration in cloth, percent dry weight	Mildew Rating after 14 Days *										
		Un-leached	Leached 24 Hrs.	No. of 20-min. washing periods					Dry-cleaned three times	Exposed Outdoors, Months		
				5	10	15	20	25		1	2	6 °
None-----	0	5	5	5	5	5	5	5	5	5	5	5
	5.00	0	0	0	0	0	0	0	0	0	0	0.5
	1.00	0	0	0	0	0	0	0.3	0	0	0	3
	0.75	0	0									
1123 *-----	0.50	0	0							0	0	
	0.25	0	0	1.7	2.0	1.0	0	0.7	0	0	0	4
	0.10	0	0							0	0	

* Code designation for alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate.

• Mildew ratings:

0=no growth.

1=trace of mildew; several spots on cloth.

2=slight mildew; up to 25% of area.

3=moderate mildew; up to 50% of area.

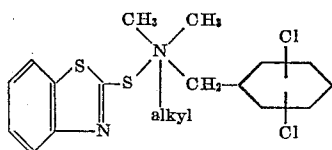
4=abundant mildew; 50-100% area covered.

5=overgrown and sporulating.

• Only the six-month exposure was obtained in a weatherometer.

exhibits optimum properties for the purposes of the invention. Both compounds are insoluble in water but are soluble in various organic solvents.

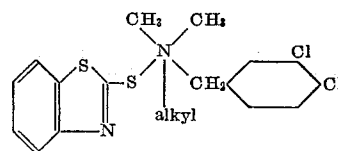
The compounds of our invention may be represented as follows:



wherein one Cl is in the 4-position and the other Cl is in a position selected from the group consisting of the 2 and 3 positions and wherein alkyl means a mixture of radicals ranging from C₈H₁₇ to C₁₈H₃₇.

The 3,4-dichlorobenzyl compound is made up into a pesticidal concentrate comprising approximately 1-50% of the said active component in any suitable non-aqueous solvent such as acetone, ethanol, benzol, chloroform, carbon tetrachloride and butyl alcohol, acetone being preferred. This concentrate may be used as such but is primarily intended as a new article of commerce which is diluted by the ultimate user to any desired extent depending upon the particular use involved and the economics of that use, and is especially useful for the treatment of textile fabrics to which it is desired to impart mildewproofing, fungicidal and germicidal properties. Such concentrate or the diluted end use product may optionally contain a mixture of the 3,4-dichloro-

The alkyl dimethyl 3,4-dichlorobenzyl ammonium mercaptobenzothiazolate may be represented by the following formula:



alkyl meaning a mixture of radicals ranging from C₈H₁₇ to C₁₈H₃₇ and predominating in lauryl, myristyl and cetyl radicals.

While we are not certain as to the explanation for the unusual activity of the above compound and do not intend to be bound by any theory concerning the same, it is believed that the combination of a germicidally active quaternary ammonium halide with the germicidally active mercaptobenzothiazole in conjunction with the dichloro substituents in the benzene ring of the benzyl group and freedom from substitution in the mercaptobenzothiazole radical produces synergism and enhancement of properties in a unique and unexpected manner representing an optimum not approached by other and even closely chemically related compounds. This is further believed to be the result of having one of the chlorine substituents in the 4- or para-position in the benzene ring of the benzyl group.

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TABLE 4

Comparison of the fungistatic activity of alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate, and its component chemicals against *Aspergillus niger*

Chemicals	Concentration in p. p. m. for Equivalent Mole Percent	Mycelial Inhibition, Percent
Components at 200 p. p. m.:		
Quaternary alone.....	153	55
Sodium MBT.....	67.4	21
		76
Quaternary-MBT.....	200	100
Components at 92 p. p. m.:		
Quaternary alone.....	70.5	33
Sodium MBT.....	31	9
		42
Quaternary-MBT.....	92	84
Components at 69 p. p. m.:		
Quaternary alone.....	52.9	26
Sodium MBT.....	23.2	6
		32
Quaternary-MBT.....	69	50

Conclusions.—The above data show that the quaternary ammonium mercaptobenzothiazolate is superior in fungistatic activity against this test organism to the additive values for the equivalent amounts of the component chemicals.

The invention is defined by the appended claims.

We claim:

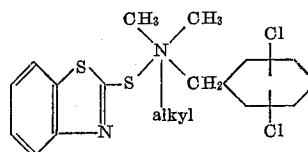
1. An alkyl dimethyl dichlorobenzyl ammonium 2-mercaptobenzothiazolate, wherein alkyl means a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

2. Alkyl dimethyl 3,4-dichlorobenzyl ammonium mercaptobenzothiazolate, wherein alkyl means a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

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3. Alkyl dimethyl 2,4-dichlorobenzyl ammonium mercaptobenzothiazolate, wherein alkyl means a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

4. A pesticidal, fungicidal and bactericidal concentrate containing 1–50% of a compound having the formula



in a non-aqueous solution one Cl being in the 4-position and the other Cl being in a position selected from the group consisting of the 2 and 3 positions and alkyl meaning a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

5. A method of rendering textile fabrics resistant to the action of fungi which comprises depositing on such textile fabrics about 0.10 to 5%, based on the dry weight of such textile fabrics, of an alkyl dimethyl dichlorobenzyl ammonium 2-mercaptobenzothiazolate, wherein alkyl means a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

6. A method of rendering textile fabrics resistant to the action of fungi which comprises applying to such textile fabrics a 1–50% solution of an alkyl dimethyl dichlorobenzyl ammonium 2-mercaptobenzothiazolate, wherein alkyl means a mixture of radicals ranging from C_8H_{17} to $C_{18}H_{37}$.

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