

PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Compositions and Method for Protecting Wool Against Damage by Insects and Microorganisms.

We, TAKEDA CHEMICAL INDUSTRIES LTD., of 27 Doshomachi 2-chome, Higashi-ku, Osaka, Japan, a Corporation organized under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composition for the protection of wool against damage by insects and microorganisms, such as fungi and bacteria, and to a method of treating wool with the composition.

Many kinds of pathological or non-pathological bacteria or fungi occur naturally and invade the human body or adhere to underwear or socks with dust or sweat, thus stimulating skin or mucous membranes to cause skin trouble. The substances decomposed by the microorganisms have an unpleasant odour which is emitted from such clothing when put on. Animal-fibres, especially wool, are often severely damaged by insects such as the Common Moth, Case Beaving Moth, Tapestry Moth, Black Carpet Beetle, Varied Carpet Beetle, Common Carpet Beetle or Fur Beetle, making the animal fibres unfit for practical use. The above-mentioned insects multiply considerably; for instance one female insect produces about 1,560,000 larvae which become imagoes after the lapse of two months to a year. The larvae eat wool continuously during this time and therefore wool must be protected from such insects and microorganisms as well as being made more durable.

Although compositions effective only against attack by insects and compositions effective only against attack by microorgan-

isms are known, at least two treatment steps are required for preventing the damage of wool by both insects and microorganisms. Thus, the wool must be treated with a composition for protection against insects and with a composition for protection against microorganisms.

The present invention provides a composition for the protection of wool against damage by insects and microorganisms which comprises as active ingredients phenyl mercuric dioctyl sulphosuccinate and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-exo-5,8-endo-dimethanona-phthalene.

Phenyl mercuric dioctyl sulphosuccinate is referred to hereinafter as PMDS and the 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4,5,8-dimethano-naphthalene is referred to hereinafter as dieldrin.

One preferred composition comprises an aqueous emulsion of 5 to 15% by weight of PMDS and 10 to 20% by weight of dieldrin.

PMDS is known to be an agent effective only against microorganisms and dieldrin is known as an agent effective only against insects, and both have been widely used. However, each one cannot prevent wool from both insects and microorganisms. It is most desirable that the preventive effect against insects and microorganisms is obtained by a single composition containing both these agents.

We have found, after careful examination, that when PMDS and dieldrin are present together in a single composition, for treating wool, the components potentiate each other and consequently, their effects are strengthened synergistically. Therefore, a composition comprising PMDS together with

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dieldrin shows stronger preventive effect on insects and microorganisms than the respective effects of PMDS and dieldrin employed separately. Furthermore, in the present invention, the preventive effect on both insects and microorganisms is obtained by only one treatment step.

Advantages of the compositions of the present invention are:—

1. The preventive effect on insects and microorganisms is very strong, compared with other compositions of this kind. For example, the composition of Example 1 is about one hundred times as effective as pentachlorophenol and 2 to 16 times as effective as bis-tributyl tin oxide.

2. The preventive effect is long-lasting. The compositions are also stable to light, heat and change the pH. Therefore the preventive effect is not substantially decreased even if wool processed by the agent of the present invention is exposed to air or sunlight, or is subjected to such treatment as vapour-pressing, ironing or cleaning.

3. The compositions are substantially harmless and do not give any stimulant to skin or mucous membrane.

4. They are colourless have no unpleasant odour and cause no irritation to the skin.

5. They do not damage the quality of wool.

6. They can easily permeate and adhere fast to wool.

PMDS and dieldrin are difficultly soluble in water, so they may be employed as an aqueous emulsion after dissolving in an organic solvent. Examples of organic solvents which may be used, are benzene, toluene, xylene, styrene, toluidine, trichloroethylene, acetone and dioxane. They may be employed solely or in admixture with one another or with other solvents such as methanol, ethanol, isopropanol, ethylene glycol, ethyl ether or chloroform. In practice, the solution may be dispersed in water to obtain an aqueous emulsion containing the active compounds. The preferable concentrations of PMDS and dieldrin vary according to the kind of woollen products and the state of the wool. In general, an emulsion which contains 5—10% by weight of dieldrin is preferably first prepared, and the emulsion is diluted with water to 300—1000 times. Of course, PMDS or dieldrin of high purity is desirable, but low purity components may be employed so long as they do not damage wool or are not injurious to the human body.

Surface active agents are preferably employed to make the emulsion. Non-ionic surface active agents, such as polyoxyethylene alkyl-phenyl ethers and polyoxyethylene sorbitol esters of mixed fatty acids, are most preferable.

Wool is treated with the thus-obtained

emulsion to obtain the preventive effect against insects and microorganisms. Generally, wool is treated by being immersed in the emulsion or by spraying the emulsion on the wool. These procedures may be carried out at room temperature or by heating to about 100° C.

The treatment according to the invention may be effected before or after wool is processed or during processing. For example, wool may be treated before or during bleaching, or before, during or after dyeing. Furthermore, the treatment may be easily conducted at home, for example, when washing or before preserving.

The following data show, by way of example the preventive effect of the compositions of the present invention on insects and microorganisms, employing:—

Emulsion A

Emulsion A consists of

PMDS	...	...	10 w/v%
dieldrin	...	...	18.5 w/v%
polyoxyethylene- ω -octyl- ω -phenylether	10		
w/v% xylene to make total volume	100		

I Preventive effect on microorganisms

(1) Fungi and Bacteria for the test:—

A mixed culture of four fungi listed on Japanese Industrial Standard for testing fungicidal activity (hereinafter abbreviated as JIS mix-fungi). A.T.C.C. and I.F.O. refer respectively to the accession numbers of the microorganisms of the American Type Culture Collection and the Institute of the Fermentation, Osaka.

<i>Aspergillus niger</i> ATCC 6275	} JIS mix-fungi
<i>Penicillium citrinum</i> ATCC 9849	
<i>Chaetomium globosum</i> ATCC 6205	
<i>Myrothecium verrucaria</i> ATCC 9095	
<i>Staphylococcus aureus</i> IFO 3061	105

(2) Sample:—

Wool-cloth which contained about 70% of water was cut into a sheet of 3 centimetres $\times$ 3 centimetres.

(3) Method of the treatment with emulsion A:—

(a) The sample was immersed for 6 seconds or 10 minutes in emulsions a, b, c, and d which were prepared by diluting the Emulsion A with water 300 times, 500 times, 700 times, and 1000 times respectively. Then the sample was squeezed until it contained 80% of water and was dried at 45—50° C. for 4 hours.

(b) The sample for washing was further immersed after the treatment (a) 3 times in a solution which comprised 0.1% of sodium carbonate and 0.2% of soap, then washed again with water.

(4) Method of the test:—

10 millilitres of 1.7% of liquid-agar were poured into a dish of 9 centimetres in diameter. After the agar had solidified, each sample which has been already treated with Emulsion A was put in the middle of the dish.

Then JIS mix-fungi or bacteria were inoculated and the medium was incubated for 1—7 days at 24—32° C.

(5) Result:—

(A) Results obtained by incubating JIS mix-fungi for 4 days

Kind of Sample	Immersion time		Dilution of Emulsion A				
			×300	×500	×700	×1000	Control
Non-washing	10 minutes	a	—	—	—	—	+++
		b	11—12	6—12	0—3	0—3	0
Non-washing	6 seconds	a	—	—	—	—	+++
		b	0—2	0—1	0—1	0—1.5	0
Washing	10 minutes	a	—	—	—	—	+++
		b	7—9	2.5—3	0.5—3	0.5	0

"a" shows whether JIS mix-fungi increased on the surface of the sample or not — means fungi did not increase on the surface of the sample.

The symbols +, ++, +++ mean respectively:—

+ Test microorganisms increase on $\frac{1}{10}$ area of the surface of the dish.

++ Test microorganisms increase on $\frac{2}{10}$ area of the surface of the dish.

+++ Test microorganisms increase on $\frac{3}{10}$ area of the surface of the dish.

"b" shows "diameter of inhibition zone (in millimetres)."

(B) Results obtained by incubating JIS mix-fungi for 7 days

Kind of Sample	Immersion time		Dilution of Emulsion A				
			×300	×500	×700	×1000	Control
Non-washing	10 minutes	a	—	—	—	—	++
		b	12	11	2	3	0
Non-washing	6 seconds	a	—	—	—	—	++
		b	1.5	1	1	1	0
Washing	10 minutes	a	—	—	—	—	++
		b	8	2.5	2.5	2.5	0

"a" and "b" have the same meaning as stated above.

(C) Results obtained by incubating *Staphylococcus aureus*

Kind of Sample	Immersion time		Dilution of Emulsion A				
			×300	×500	×700	×1000	Control
Non-washing	10 minutes	a	—	—	—	—	+
		b	24—30	20—30	10—30	6—8	0
Non-washing	6 seconds	a	—	—	—	—	+
		b	10—18	3—6	1—5	0.5—5	0
Washing	10 minutes	a	—	—	—	—	+
		b	10—11	8—9	2—8	2—3	0

"a" shows whether *Staphylococcus aureus* increased or not.

"b" has the same meaning as stated above.

II. Preventive effect on insects

(1) Larvae of Black Carpet Beetle (*Attagenus Piceus* Oliver) were fed with pupa-powder for 110 days.

(2) Sample:—
Muslin which contained about 70% of water.

(3) Method of the treatment with Emulsion A:—

(a) The sample was immersed for 6 seconds or 10 minutes in the emulsions *a*, *b*, *c* and *d* which were prepared by diluting the emulsion A with water 300 times, 500 times, 700 times and 1000 times, respectively.

(b) The sample for washing was further immersed after the treatment (a), 3

times in a solution which contained 0.1% of sodium carbonate and 0.2% of soap, then was washed again with 20 water.

(4) Method of the test:—

Each sample which had been treated with Emulsion A was cut into a sheet of 2 centimetres by 2 centimetres and was put, together with 9 insects, in a small dish 4.5 centimetres in diameter and 1.5 centimetres high. Then the dishes were kept at the constant temperature of $25 \pm 0.5^\circ \text{C}$. and at the constant relative humidity of $70 \pm 5\%$ for 15 days.

(5) Result:—

(A) Non-washing

Immersion time	Dilution of the composition	Number of the live-insects	Number of the dead insects	Number of the poisoned insects (after 7 days)	Weight eaten by insects (milli-gram)
10 minutes	$\times 300$	6	3	7	0
	$\times 500$	7	2	7	0.5
	$\times 700$	7	2	7	0.3
	$\times 1000$	6	3	7	0
6 seconds	$\times 300$	6	3	6	0
	$\times 700$	5	4	7	0
	$\times 500$	8	1	7	0
	$\times 1000$	7	2	4	0
Control		9	0	0	6.7

Poisoned insect means an insect which reposed by bending its abdomen inwards, and responded only slightly when being touched by tweezers.

(B) Washing

Immersion time	Dilution of the composition	Number of the live-insects	Number of the dead insects	Number of the poisoned insects (after 7 days)	Weight eaten by insects (milli-gram)
10 minutes	$\times 300$	5	4	7	0.3
	$\times 500$	9	0	4	0
	$\times 700$	8	1	5	0
	$\times 1000$	8	1	2	0.5
6 seconds	$\times 300$	7	2	5	0
	$\times 500$	9	0	4	0.5
	$\times 700$	9	0	4	0.5
	$\times 1000$	9	0	4	0.5
Control		9	0	0	8.0

The following Examples illustrate the invention:—

EXAMPLE 1.

A preferred composition consisted of:—

- | | | |
|----|-------------------------------|-----------|
| 5 | Phenyl mercuric dioctyl sul- | |
| | phosuccinate... | 10 w/v% |
| | Dieldrin ... | 18.5 w/v% |
| | Polyoxyethylene nonyl phenyl- | |
| | ether ... | 20 w/v% |
| 10 | Xylene to total volume ... | 100 |

EXAMPLE 2.

An aqueous emulsion was prepared by diluting the emulsion obtained in Example 1 with water. Woollen-underwear was immersed in the thus-obtained aqueous emul-

- 15 sion just after washing.

WHAT WE CLAIM IS:—

1. A composition for the protection of wool against damage by insects and micro-organisms, which comprises, as active ingredients phenyl mercuric dioctyl sulphosuccinate and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-exo-5,8,-endodimethanonaphthalene.

- 25 2. A composition for the protection of

wool against damage by insects and micro-organisms, which comprises an aqueous emulsion of phenyl mercuric dioctyl sulphosuccinate and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-exo-5,8-endodimethanonaphthalene.

3. A composition as claimed in Claim 2, which comprises 5—15% by weight of phenyl mercuric dioctyl sulphosuccinate and 10—20% by weight of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-exo-5,8-endo-dimethano-naphthalene.

4. A method of protecting wool against damage by insects and microorganisms, which comprises treating the wool with the composition claimed in any of the preceding claims.

5. A method as claimed in Claim 4 substantially as described.

6 Wool when treated by the process claimed in Claim 4 or Claim 5.

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The following Examples illustrate the invention:—

EXAMPLE 1.

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| 10 | Xylene to total volume ... | 100 |

EXAMPLE 2.

- 15 An aqueous emulsion was prepared by diluting the emulsion obtained in Example 1 with water. Woollen-underwear was immersed in the thus-obtained aqueous emulsion just after washing.

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