

1191112



PATENT SPECIFICATION

NO DRAWINGS

1191112

Date of Application (No. 20959/67) and filing Complete Specification: 5 May, 1967.

Application made in Switzerland (No. 6667) on 6 May, 1966.

Complete Specification Published: 6 May, 1970.

Index at acceptance:—C2 C(1E4K1, 1E4K4, 1E5K1, 1E5K4, 1G5A, 1G5B, 1G5C, 1G6A1, 1G6B3, 1G6B4, 1K1C3, 1K1D, 1K1E, 1Q1A, 1Q3, 1Q6B1, 1Q6C, 1Q7A, 1Q8A, 1Q8B, 1Q8C, 1Q9C, 1Q9L, 1Q11C, 1Q11D, 1Q11G, 1Q11H, 1Q11J, 213, 22Y, 220, 25Y, 250, 252, 305, 31Y, 313, 332, 337, 338, 34Y, 342, 579, 601, 62X, 621, 631, 661, 681, 708, 79Y, 791, 183—199—283, KF, MM); A5 E(1C4B2, 1C4B3, 1C4B4, 1C17)

International Classification:—C 07 d 49/38

COMPLETE SPECIFICATION

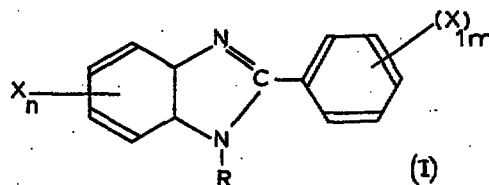
New Benzimidazoles, their production and use

We AGRIPAT S.A. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, 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:—

The present invention concerns new substituted benzimidazole derivatives having insecticidal properties and, in particular, insecticidal and acaricidal agents which contain these new benzimidazole derivatives as active substances and, in particular, serve to combat keratin-eating insects and their larvae, as well as the use of these active substances and the agents containing them for combatting insects and spiders, in particular however, for the protection of keratin materials from attack by such insects.

Of the benzimidazole derivatives known today, those containing a low molecular halogenoalkyl radical in the 2-position have been suggested as herbicidal and pesticidal active substances for combatting weeds, insects, nematodes and mites (Dutch application open to public inspection 64/10413; Angew. Chem. 77 (1965) pages 814 and 911—912). These literature citations make no mention of a keratin-protecting action of these substances. These 2-halogen-alkyl-benzimidazoles, if they are polyhalogenated in the nucleus, have marked toxicity to warm blooded animals which limits their possibilities of application.

It has now been found that new substituted 2-phenyl-benzimidazoles of the general formula I



wherein

R represents hydrogen or a metal cation, each of the symbols X and X₁ represents fluorine, chlorine or bromine, particularly chlorine or bromine, a trifluoromethyl group, an alkyl or alkoxy radical, a nitro, hydroxyl or amino group, an alkanoylamino group, a substituted or unsubstituted phenoxy or phenylsulphonyl group or the radical of a sulphonic acid or its amide or ester forms, n represents a whole number from 1 to 4 and

m represents a whole number from 1 to 5, with the condition that, in all, at least 3 of the substituents symbolised by X and X₁ are halogen atoms and/or trifluoromethyl radicals of which, however, none is in the o-position to the linking position in the phenyl radical in 2-position and that there are, at most, 2 trifluoromethyl groups in each of the two benzene nuclei of the molecule, have excellent insecticidal and acaricidal properties, in particular, a marked action against insects which eat keratin material and their stages of development such as against the larvae of moths and other small butterflies, also fur and carpet beetle larvae. For this reason the new active substances of general formula I are particularly suitable for the protection of

keratin material, such as wool and articles containing wool, from attack by such pests. Active substances of the general formula I have not been described in the literature.

5 The strength of action of the new benzimidazole derivatives of general formula I depends substantially on the degree of their substitution by halogen atoms and/or trifluoromethyl groups, for which reason at least three
10 such substituents must be present in the molecule in order to attain a satisfactory insecticidal action. Generally, the activity increases as the number of halogen and CF_3 substituents is raised. Compared with known halogenated and/or trifluoromethylated 2-trifluoromethylbenzimidazoles which have been suggested as
15 pesticidal active substances (Angew. Chem. 77 (1965) pages 814 and 911—912), the new compounds, whilst having about the same number of halogen substituents in the condensed benzene ring, have much less toxicity to warm blooded animals. For example, the
20 toxicity DL_{50} of the known 4,5,6,7-tetrachloro-2-trifluoromethyl-benzimidazole to rats *per os* is less than 10 mg/kg whereas this DL_{50} of the 4,5,6,7-tetrachloro-2-(3',4'-dichlorophenyl)-benzimidazole according to the invention is higher than 5000
25 mg/kg.

30 Compounds of the general formula I where R is hydrogen are acids which are capable of forming salts e.g. with alkali and alkaline earth metal hydroxides and the corresponding carbonates, in which salts R is the monovalent equivalent of a metal cation. Preferred salts
35 are the soluble alkali metal salts, particularly the sodium and potassium salts.

All substituents X and X_1 can be the same or different but at least three of them must
40 be halogen atoms of an atomic weight below 100 and/or trifluoromethyl groups. The preferred halogen substituents are chlorine and bromine. In principle, each halogen substituent can be replaced by a trifluoromethyl
45 group but in practice it is not possible to build in more than 2 trifluoromethyl groups in each of the two benzene nuclei of the molecule. In the phenyl radical, no halogen atom or CF_3 group may be in *ortho*-position to the
50 linking position to the benzimidazole structure as otherwise the insecticidal activity is lost in practice. For the other radicals represented by X and X_1 the limitation given above for the *ortho*-position to the phenyl radical
55 is not valid. The benzene nuclei are preferably monosubstituted by the other substituents. As the preferred alkyl, alkoxy and alkanoylamino radicals represented by X and X_1 are meant such radicals having 1 to 5 carbon atoms in
60 their alkyl moiety, as in particular the methyl, methoxy and acetylamino radical. By substituted phenoxy and phenylsulphonyl radicals are intended such radicals which are substituted preferably by at least one halogen
65 atom and/or one CF_3 group. Also the sul-

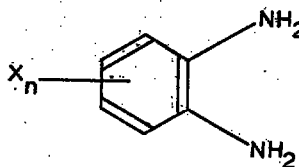
phonic acid group ($-\text{SO}_3\text{H}$) and its amide and ester forms can be used as such substituents.

The new active substances have excellent affinity to keratin fibres. Due to their affinity
70 to keratin fibres, the 2-phenyl-benzimidazole derivatives of general formula I draw from aqueous dispersions and, also from aqueous solutions of their salts, onto these fibres and in this way protect keratin material treated
75 therewith from injury caused by moth larvae and other small butterflies as well as from injury caused by the larvae of the fur and carpet beetles (*Anthrenus* and *Attagenus*).

The active substances of general formula I are also active, however, against other insects, including termites, and also mites, and can thus be used generally in plant protection, particularly for the industrial application
80 in plant protection and protection of materials, e.g. for the protection of organic materials such as paper, wood, textiles, and plastics from attack by insects and mites.

The new benzimidazole derivatives of general formula I can be produced by the following methods:

a) *o*-Phenylenediamines optionally substituted by radicals X of the formula



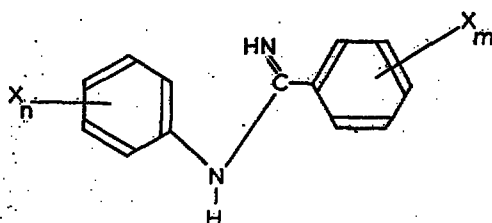
are condensed e.g. in the melt, optionally in
95 the presence of catalysts such as mineral acids, polyphosphoric acid or metaphosphoric acid esters, with optionally substituted benzoic acids or with their esters, amides, acid halides and nitriles, and optionally, subsequently
100 chlorinated or brominated in at least one benzene nucleus, preferably in dimethyl formamide as solvent.

The new 2-phenyl-benzimidazoles are also obtained by a variation of this process when the *o*-phenylenediamines mentioned above are
105 reacted with the corresponding benzaldehydes in the presence of an oxidising agent such as copper acetate or nitrobenzene instead of with benzoic acid derivatives.

b) The new 2-phenyl-benzimidazoles can also be obtained by reductive cyclisation, e.g. with zinc and hydrochloric acid, of correspondingly substituted N-benzoyl-*o*-nitranilines. This cyclisation can also be performed in
110 steps. This method is of particular interest if the usual cyclisation methods are made difficult due to the presence of a sterically hindered specific substituent X. Starting from *o*-chloronitrobenzenes, first *o*-nitranilines are produced and then acylated in the amino
115 group with a reactive benzoic acid derivative and in this way the N-benzoyl-*o*-nitranilines
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are obtained as starting materials for the reductive cyclisation. The cyclised 2-phenyl-benzimidazoles can then be halogenated in the benzene nuclei.

- 5 c) Finally, the new active substances of general formula I can also be obtained by oxidative cyclisation of optionally substituted N-phenyl-benzamidines of the formula



- 10 Preferably a hypochlorite is used as oxidising agent. In this method it is better to use un-halogenated or only slightly halogenated benzamidines as starting materials and, after cyclisation, to halogenate the products obtained.

15 The latter method of oxidative cyclisation of N-phenyl-benzamidines is of particular interest if the nitranilines and 1,2-phenylenediamines necessary for the production methods described above are difficultly accessible.

- 20 Elementary chlorine and bromine in particular are used for the halogenation of the 2-phenyl-benzimidazoles in order to introduce halogen or to increase the halogen substitution.
- 25 Water, aromatic hydrocarbons, halogenated hydrocarbons, N-alkylated acid amides and alcohols, e.g. methanol or glycol monomethyl ether can be used as solvents or diluents for the halogenation. The halogenation is performed in aqueous medium with elementary chlorine or with nascent chlorine from hydrogen chloride in the presence of oxidising agents, or with elementary bromine and bromate in the presence of dilute acid. Sulphuryl chloride is the principle example of an agent which gives off nascent chlorine.

- 30 Halogenation of the benzimidazoles with elementary chlorine or bromine in an N-alkylated organic acid amide, particularly dimethyl formamide, optionally in the presence of a catalyst, at temperatures between 0 and 100°C., is preferred.

- 35 The following examples describe the production of the new active substances of general formula I. Where not otherwise stated, parts are given as parts by weight and the temperatures are given in degrees Centigrade.

EXAMPLE 1

- 40 2 - (3',5' - bis - trifluoromethyl - phenyl) - 4,5,6,7 - tetrachloro - benzimidazole

- 50 a) 16.2 Parts of 1,2-phenylenediamine are dissolved in 100 parts of metaphosphoric acid triethyl ester while stirring and heating to 100°. 26 Parts of 3,5-bis-trifluoromethyl benzoic acid are then added and the mixture is heated for 1 hour at 120°. After cooling to

50°, 1500 parts of water are added and the suspension so formed is made weakly alkaline (pH=8) by the addition of solid sodium bicarbonate. The product is filtered, washed, dried and dissolved in ethanol. The side product, the diamide of *o*-phenylenediamine, which in practice is insoluble in ethanol, is removed and the 2-(3',5'-bis-trifluoromethyl-phenyl)-benzimidazole is crystallised from aqueous alcohol: M.P. 218—219°.

b) 18 Parts of chlorine are introduced over a period of 2 hours into a 60° hot solution of 6.6 parts of 2-(3',5'-bis-trifluoromethyl-phenyl)-benzimidazole and 0.1 parts of iron-III chloride in 100 parts by volume of dimethyl formamide. The reaction mixture is then added to 2000 parts by volume of water while stirring vigorously. The precipitate formed is filtered off, washed with water and then dried. The 2 - (3',5' - bis - trifluoromethyl - phenyl) - 4,5,6,7 - tetrachloro - benzimidazole melts at 278.5—279°.

EXAMPLE 2

- 2 - (3',4' - dichlorophenyl) - 4,7 - dibromo-5,6 - dichloro - benzimidazole

a) A finely pulverised mixture of 18.7 parts of 4,5-dichloro-*ortho*-phenylenediamine and 19.1 parts of 3,4-dichloro-benzoic acid is heated for 1 hour at 120—130° with 120 parts of metaphosphoric acid ethyl ester, while stirring. 2000 Parts of water are added to the cold reaction product and the suspension so obtained is made alkaline with solid sodium bicarbonate. The product is filtered off, dried and recrystallised from ethanol.

The 2 - (3',4' - dichlorophenyl) - 5,6-dichloro-benzimidazole obtained melts at 251—252°.

b) 10 Parts of 2 - (3',4' - dichlorophenyl) - 5,6 - dichloro - benzimidazole are suspended in 200 parts of water and 3 parts of concentrated sulphuric acid are added. The whole is brought to the boil and simultaneously 8 parts of bromine and also a solution of 4.2 parts of potassium bromate in 60 parts of water are added dropwise within about 1 hour. The whole is then refluxed for 10 hours, again the amounts of bromine and bromate solution given above are added dropwise and the whole is refluxed for another 10 hours. Excess bromine is then distilled off and the reaction product, when cold, is filtered off under suction. The crude product is dissolved in a mixture of 2N sodium hydroxide solution and ethanol, the filtrate is acidified with dilute hydrochloric acid and the precipitate is filtered off, dried and recrystallised from ethanol. The 2 - (3',4' - dichlorophenyl) - 4,7 - dibromo - 5,6 - dichloro - benzimidazole melts at 269—270°.

EXAMPLE 3

- 2 - (3',4',5' - trichlorophenyl) - 4,6 - bis-trifluoromethyl - benzimidazole

a) A mixture of 6.9 parts of 3,5-bis-trifluoromethyl aniline, 6.2 parts of 3,4,5-tri-

chlorobenzonitrile and 4.2 parts of anhydrous zinc chloride is heated for 3 hours at 180°. The cold melt is dissolved with warm alcohol, water and chloroform are added, the chloroform phase is removed, dried with MgSO₄, the chloroform is evaporated in vacuo and the residue is recrystallised from hexane.

5 The N - (3,5 - bis - trifluoromethyl-phenyl) - 3',4',5' - trichlorobenzamidine so
10 obtained crystallises into needles which melt at 148—151°.

15 b) 17.4 Parts of this benzamidine are dissolved in 150 parts by volume of methanol and 80 parts by volume of 1N HCl are added. 28 Parts by volume of 1.5 molar NaOCl solution are then added dropwise at room temperature and the whole is stirred for 10 minutes. The reaction milieu is made
20 alkaline by the addition of 7.5 parts of sodium carbonate and then the whole is refluxed for 30 minutes. After evaporation of the methanol, the reaction product is isolated and recrystallised from methanol. The 2-(3',4',5'-trichlorophenyl) - 4,6 - bis - trifluoromethyl-

benzimidazole is obtained in this way as silky needles which melt at 188—190°.

EXAMPLE 4

2 - (3',4' - dichlorophenyl) - 4,5,6,7 - tetrachloro - benzimidazole

A mixture of 12.3 parts of tetrachloro-*o*-phenylene-diamine, 10.5 parts of 3,4-dichlorobenzoyl chloride and 50 parts by volume of 25% hydrochloric acid is heated in a bomb tube for 40 minutes at 180—185°. After cooling, dilute sodium hydroxide solution and alcohol are added to the reaction mixture and the alkaline solution of the reaction product is treated with animal charcoal and filtered. Dilute hydrochloric acid is added to the filtrate and the precipitate formed is filtered off under suction and washed with water. After recrystallisation from alcohol, the end product melts at 277—278°.

The following benzimidazole derivatives of general formula I are produced in a manner analogous to those described in the above examples:

TABLE I

Compound	M.P.
2-(3'-chlorophenyl)-4,5,6,7-tetrachloro-benzimidazole	322—324°
2-(4'-chlorophenyl)-4,5,6,7-tetrachloro-benzimidazole	265—270°
2-(3'-bromophenyl)-4,5,6,7-tetrachloro-benzimidazole	327—330°
2-(3'-chlorophenyl)-4,5,6,7-tetrabromo-benzimidazole	320—322°
2-(4'-chlorophenyl)-4,5,6,7-tetrabromo-benzimidazole	277—279°
2-(3'-bromophenyl)-4,5,6,7-tetrabromo-benzimidazole	325—328°
2-(4'-bromophenyl)-4,5,6,7-tetrabromo-benzimidazole	253—256°
2-(3'-trifluoromethyl-phenyl)-4,5,6,7-tetrachlorobenzimidazole	321—323°
2-(4'-trifluoromethyl-phenyl)-4,5,6,7-tetrachlorobenzimidazole	274—276°
2-(4'-nitrophenyl)-4,5,6,7-tetrachloro-benzimidazole	317—193°
2-[4'-(<i>p</i> -chlorophenoxy)-phenyl]-4,5,6,7-tetrachloro-benzimidazole	246—248°
2-(3',5'-dinitrophenyl)-4,5,6,7-tetrachloro-benzimidazole	362—364°
2-(3',4'-dimethyl-phenyl)-4,5,6,7-tetrachloro-benzimidazole	290—293°
2-(3',4'-dichlorophenyl)-4,5,6,7-tetrabromo-benzimidazole	282—283°
2-(3',5'-bis-trifluoromethyl-phenyl)-4,5,6,7-tetrabromo-benzimidazole	285—286°
2-(3',4',5'-trichlorophenyl)-4,5,6,7-tetrachlorobenzimidazole	297—300°

TABLE I (Continued)

Compound	M.P.
2-(3',4',5'-trimethoxy-phenyl)-4,5,6,7-tetrachlorobenzimidazole	310—311°
2-(4'-chlorophenyl)-4,5,6,-trichloro-7-bromo-benzimidazole	258—259°
2-(3',4'-dichlorophenyl)-4,5,6-trichloro-7-bromobenzimidazole	274—276°
2-(2'-hydroxy-3',5'-dichlorophenyl)-4,5,7-trichloro-benzimidazole	262—264°
2-(3',4'-dichlorophenyl)-6-bromo-4,5,7-trichlorobenzimidazole	270—273°
2-(3',4'-dichlorophenyl)-4,6,7-trichloro-benzimidazole	292—293°
2-(3'-trifluoromethyl-4'-chlorophenyl)-4,6,7-trichloro-benzimidazole	262—264°
2-(3',4'-dichlorophenyl)-4,6,7-trichloro-5-fluorobenzimidazole	268—270°
2-(3',4'-dichlorophenyl)-4,6,7-trichloro-5-acetylamino-benzimidazole	230—250°
2-(3',5'-bis-trifluoromethyl-phenyl)-4,6,7-tribromo-5-trifluoromethyl-benzimidazole	243—246°
2-(3',4'-dichlorophenyl)-4,6-dichloro-7-(<i>p</i> -chlorophenyl-sulphonyl)-benzimidazole	302—304°
2-(3',4'-dichlorophenyl)-4,6-dibromo-7-chloro-5-trifluoromethyl-benzimidazole	214—215°
2-(3',4'-dichlorophenyl)-4,7-dibromo-5,6-dichlorobenzimidazole	268—270°
2-(3',4'-dichlorophenyl)-5,6-dichloro-benzimidazole	251—252°
2-(3',4'-dichloro-2'-sulphonyl-phenyl)-5,6-dichloro-benzimidazole	>360°
2-(3',5'-bis-trifluoromethyl-phenyl)-5-trifluoromethyl-4,6-dibromo-7-chlorobenzimidazole	212—215°
2-(3',4'-dichlorophenyl)-5-trifluoromethyl-benzimidazole	223—225°
2-(3',5'-bis-trifluoromethyl-phenyl)-5-trifluoromethyl-benzimidazole	224—226°

The new active substances of general formula I can be applied by the usual processes for textile finishing. They have considerable affinity to keratin material and are thus excellently suitable for the protection thereof from insects which eat it, particularly for the washproof mothproofing of such materials but in the raw and in the processed state, e.g. of raw or processed sheep's wool as well as other animal hairs, fells, feathers and furs. Compared with other active substances of the benzimida-

zole series, the new active substances of general formula I are distinguished by their good stability to washing.

In addition to their insecticidal activity against the larvae of the clothes moth, the compounds of formula I also have such an action against the larvae of the fur and carpet beetles so that textiles such as blankets, woollen carpets, woollen underwear, woollen outer clothes and knitted goods treated in any way desired with agents containing the

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new active substances are given lasting protection against all types of insects which injure keratin fibres by eating.

- 5 The testing of benzimidazoles of general formula I according to the invention as to their insecticidal action against such insects which eat keratin fibres and the testing of keratin textile materials treated with these active substances as to their resistance to attack from such pests were performed in the following way:

Test methods and results

- 15 A 0.5% by weight stock solution of the active substance to be tested in 2-methoxyethanol is prepared. Then, at room temperature, an aqueous application liquor is produced which, in 400 ml, contains 20 ml of the said stock solution (0.1 g active substance). 10 g of wool flannel are then well wetted with hot water and introduced at room temperature. While constantly circulating the wool sample, the bath temperature is raised to 60° within 20 15 minutes, then 2% of formic acid (80%), calculated on the weight of the wool, are added and the sample is treated for another 30 minutes at this temperature in this liquor. It is then cooled, the wool sample is rinsed in running tap water, centrifuged and hung up to dry. The concentration of active substance

is 1% calculated on the weight of the wool. 30

The sample so dried is then subjected to a mothproofing test against clothes moths (*Tineola biselliella*) according to the prescription of the "Schweiz. Normenverbandes SNV 95901" (Swiss Association for Standardisation, SNV 95901), and the fastness is tested against larvae of the fur beetle (*Attagenus piceus*) and the carpet beetle (*Anthrenus vorax*) according to SNV 95902; obviously, the method for *Anthrenus* larvae was applied to *Attagenus piceus* larvae by using 6—7 week old larvae of the latter type for the test. The method consists in cutting 4 pieces of equal size from the treated wool flannel sample and exposing each of these pieces for 14 days at a constant temperature (28°C.) and constant relative humidity (65%) to attack (by eating) of 15 larvae of the corresponding pest (in each case 2 pieces exposed to the same pest). 40 45 50

The results are given in the following table.

The evaluation is based on the loss in weight of the flannel sample and is shown in the Table as follows: 55

xxxx very good action
xxx good action
xx moderate action
x bad action.

TABLE II

(1% active substance calculated on the weight of the wool)

active substance	moths	Attagenus	Anthrenus
2-(4'-chlorophenyl)-4,5,6,7-tetrachloro-benzimidazole	xxxx	xxx	xxxx
2-(4'-trifluoromethyl-phenyl)-4,5,6,7-tetrachloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichloro-phenyl)-4,5,6,7-tetrachloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-4,5,6,7-tetrabromobenzimidazole	xxxx	xxx	xxxx
2-(3',5'-bis-trifluoromethylphenyl)-4,5,6,7-tetrachlorobenzimidazole	xxxx	xxxx	xxxx
2-(3',5'-bis-trifluoromethylphenyl)-4,5,6,7-tetrabromobenzimidazole	xxxx	xxxx	xxxx
2-(3',4',5'-trichlorophenyl)-4,5,6,7-tetrachloro-benzimidazole	xxxx	xxxx	xxxx
2-(4'-chlorophenyl)-4,5,6-trichloro-7-bromobenzimidazole	xxxx	xxxx	xxxx

TABLE II (Continued)

Active substance	moths	Attagenus	Anthrenus
2-(3',4'-dichlorophenyl)-4,5,6-trichloro-7-bromo-benzimidazole	xxxx	xxx	xxx
2-(3',4'-dichlorophenyl)-6-bromo-4,5,7-trichloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-4,6,7-trichloro-benzimidazole	xxxx	xxxx	xxxx
2-(3'-trifluoromethyl-4'-chlorophenyl)-4,6,7-trichloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-4,6,7-trichloro-5-fluoro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4',5'-trichlorophenyl)-4,6-bis-trifluoromethylbenzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-5-trifluoromethyl-4,6-dibromo-7-chloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-4,7-di-bromo-5,6-dichloro-benzimidazole	xxxx	xxxx	xxxx
2-(3',4'-dichlorophenyl)-5-trifluoromethylbenzimidazole	xxxx	xxxx	xxxx

5 Insecticidal and acaricidal agents according to the invention which contain the new active substances and can be used in, e.g. plant protection can be in solid or liquid form, e.g. dusts, sprinkling agents or aqueous dispersions which are obtained from wettable powders, pastes or emulsion concentrates, and solutions and aerosols.

10 For the protection of keratin material from insects which eat it, the agents according to the invention should contain the new active substances in a finely distributed form. Thus, solutions, aqueous suspensions and emulsions are used in particular for this application.

15 The active substance of general formula I in the form of their alkali metal salts generally have good water solubility. They can be brought onto keratin material direct from these aqueous solutions by dipping such material for a shorter or longer time in solutions of the alkali metal salts, or spraying it with the solutions or treating it therein at a raised temperature.

25 The keratin protection agents according to the invention can contain other known active substances in addition to the new active substances of general formula I. They can be combined, e.g. with halogenated anthranilic acid anilides, with halogenated diphenyl ureas, with halogenated and sulphonated phenoxy-diphenyl ureas and with 2-chloromethyl-sulphonylamino polychlorodiphenyl ethers.

The agents according to the invention are produced in the known way by intimately mixing the active substances with solid or liquid carriers and distributing agents. For the protection of keratin material, particularly organic solvents have proved valuable such as: propylene glycol, methoxyethanol, ethoxyethanol and dimethyl formamide. As distributing agents, emulsifying agents (including surface active agents, e.g. sulphated castor oil, sulphite waste liquor and fatty alcohol sulphates can be used.

Keratin materials can be impregnated with the active substances by the most varied textile finishing processes such as hot or cold, aqueous dye, chroming, pad dyeing or after-treatment baths. The new active substances are fixed onto the keratin fibre not only by hot application but also by cold application.

Because of the good solubility in organic solvents, the active substances are also well suitable for application from non-aqueous media. Here, the materials to be protected can simply be impregnated with the solutions. With a suitable choice of solvent, the materials can be given an insecticidal finish also in a dry cleaning process.

The production and composition of agents according to the invention and their application for the protection of keratin materials from pests which eat it, are further illustrated in the following examples. Parts are given

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therein as parts by weight and the temperatures are in degrees Centigrade.

EXAMPLE I

0.5 Parts of 2-(3',4'-dichlorophenyl)-4,5,6,7-tetrachloro-benzimidazole in the form of the sodium salt are dissolved with the aid of 10 parts of 0.1N sodium hydroxide solution and a little ethanol. This solution is diluted with 3000 parts of water and 100 parts of wool are treated for 15 minutes in this liquid at 60°. 5 Parts of 10% acetic acid are then added and the treatment is continued at 60° for another hour. The wool is then rinsed in the usual way and dried. On testing, it proves to be resistant to attack by moth larvae, fur and carpet beetle larvae.

EXAMPLE II

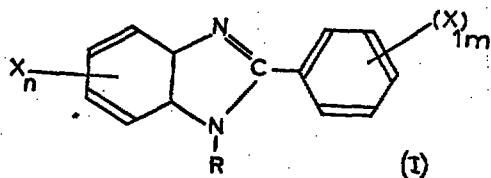
First, a 20% solution of 2-(4'-chlorophenyl)-4,5,6-trichloro-7-bromo-benzimidazole in 2-methoxyethanol is produced. 10 Parts by volume of this solution are diluted with 200 parts by volume of a solvent suitable for dry cleaning, e.g. a suitable benzine fraction ("Diluan S"). If desired, cleansing additives can be added. In addition, the compounds can also be used in the form of the alkali metal salts or can be converted into such in the solution by the addition of a slight amount of alkali liquor. The wool articles are treated in the usual way in this cleaning liquor and then centrifuged to a solvent content of about 100% of the weight of the wool. After drying, they prove to be mothproofed.

The same bath or those of analogous composition can be used in an analogous way for the mothproofing of untreated keratin-containing articles or of those which have been treated in some way or cleaned.

Similar mixtures can also be used for the sprinkling or spraying of wool in any stage of processing.

WHAT WE CLAIM IS:—

1. Substituted 2-phenyl-benzimidazoles of the general formula I



wherein

R represent hydrogen or a metal cation, each of the symbols X and X₁ represents fluorine, chlorine or bromine, a trifluoromethyl group, an alkyl or alkoxy radical, a nitro, hydroxyl or amino group, an alkanoylamino group, a substituted or unsubstituted phenoxy or phenylsulphonyl group or the radical of a sulphonic acid or its amide or ester forms,

n represents a whole number from 1 to 4, and

m represents a whole number from 1 to 5, with the proviso that, in all, at least three of the substituents symbolised by X and X₁ are halogen atoms and/or trifluoromethyl radicals of which, however, none is in an *ortho* position to the linking position to the phenyl radical in the 2 position and that there are at most 2 trifluoromethyl groups present in each of the two benzene nuclei of the molecule.

2. The compound 2-(3',4'-dichlorophenyl)-4,5,6,7-tetrachloro-benzimidazole.

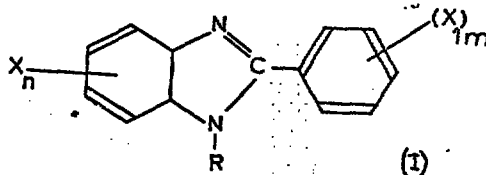
3. The compound 2-(3',5'-bis-trifluoromethyl-phenyl)-4,5,6,7-tetrachloro-benzimidazole.

4. The compound 2-(3',5'-bis-trifluoromethyl-phenyl)-4,5,6,7-tetrabromo-benzimidazole.

5. The compound 2-(3',4'-dichlorophenyl)-4,6-dibromo-5-trifluoromethyl-7-chloro-benzimidazole.

6. The compound 2-(3',5'-bis-trifluoromethyl-phenyl)-4,6-dibromo-5-trifluoromethyl-7-chloro-benzimidazole.

7. Insecticidal and acaricidal agent, characterised in that it contains, as active substance, a substituted 2-phenyl-benzimidazole of the general formula I



wherein

R represents hydrogen or a metal cation, each of the symbols X and X₁ represents fluorine, chlorine or bromine, a trifluoromethyl group, an alkyl or alkoxy radical, a nitro, hydroxyl or amino group, an alkanoylamino group, a substituted or unsubstituted phenoxy or phenylsulphonyl group or the radical of a sulphonic acid or its amide or ester forms,

n represents a whole number from 1 to 4, and

m represents a whole number from 1 to 5, with the proviso that, in all, at least three of the substituents symbolised by X and X₁ are halogen atoms and/or trifluoromethyl radicals of which, however, none is in the *ortho* position to the linking position to the phenyl radical in the 2-position and that there are at most 2 trifluoromethyl groups present in each of the two benzene nuclei of the molecule.

8. Agent according to claim 7, characterised in that it contains the active substances of formula I in finely distributed form and in admixture with suitable solid or liquid distributing agents, including surface active agents.



therein as parts by weight and the temperatures are in degrees Centigrade.

EXAMPLE I

- 0.5 Parts of 2-(3',4'-dichlorophenyl)-4,5,6,7-tetrachloro-benzimidazole in the form of the sodium salt are dissolved with the aid of 10 parts of 0.1N sodium hydroxide solution and a little ethanol. This solution is diluted with 3000 parts of water and 100 parts of wool are treated for 15 minutes in this liquid at 60°. 5 Parts of 10% acetic acid are then added and the treatment is continued at 60° for another hour. The wool is then rinsed in the usual way and dried. On testing, it proves to be resistant to attack by moth larvae, fur and carpet beetle larvae.

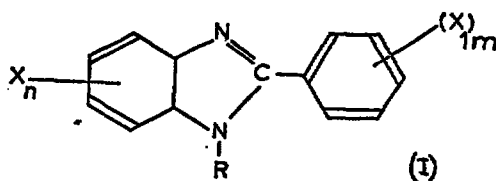
EXAMPLE II

- First, a 20% solution of 2-(4'-chlorophenyl)-4,5,6-trichloro-7-bromo-benzimidazole in 2-methoxyethanol is produced. 10 Parts by volume of this solution are diluted with 200 parts by volume of a solvent suitable for dry cleaning, e.g. a suitable benzene fraction ("Diluan S"). If desired, cleansing additives can be added. In addition, the compounds can also be used in the form of the alkali metal salts or can be converted into such in the solution by the addition of a slight amount of alkali liquor. The wool articles are treated in the usual way in this cleaning liquor and then centrifuged to a solvent content of about 100% of the weight of the wool. After drying, they prove to be mothproofed.

- The same bath or those of analogous composition can be used in an analogous way for the mothproofing of untreated keratin-containing articles or of those which have been treated in some way or cleaned. Similar mixtures can also be used for the sprinkling or spraying of wool in any stage of processing.

WHAT WE CLAIM IS:—

1. Substituted 2-phenyl-benzimidazoles of the general formula I



wherein

- R represent hydrogen or a metal cation, each of the symbols X and X₁ represents fluorine, chlorine or bromine, a trifluoromethyl group, an alkyl or alkoxy radical, a nitro, hydroxyl or amino group, an alkanoylamino group, a substituted or unsubstituted phenoxy or phenylsulphonyl group or the radical of a sulphonic acid or its amide or ester forms,

n represents a whole number from 1 to 4, and

m represents a whole number from 1 to 5, with the proviso that, in all, at least three of the substituents symbolised by X and X₁ are halogen atoms and/or trifluoromethyl radicals of which, however, none is in an *ortho* position to the linking position to the phenyl radical in the 2 position and that there are at most 2 trifluoromethyl groups present in each of the two benzene nuclei of the molecule.

2. The compound 2 - (3',4' - dichlorophenyl) - 4,5,6,7 - tetrachloro - benzimidazole.

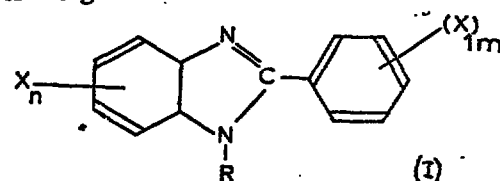
3. The compound 2 - (3',5' - bis - trifluoromethyl - phenyl) - 4,5,6,7 - tetrachloro-benzimidazole.

4. The compound 2 - (3',5' - bis - trifluoromethyl - phenyl) - 4,5,6,7 - tetrabromo-benzimidazole.

5. The compound 2 - (3',4' - dichlorophenyl) - 4,6 - dibromo - 5 - trifluoromethyl - 7 - chloro - benzimidazole.

6. The compound 2 - (3',5' - bis - trifluoromethyl - phenyl) - 4,6 - dibromo - 5 - trifluoromethyl - 7 - chloro - benzimidazole.

7. Insecticidal and acaricidal agent, characterised in that it contains, as active substance, a substituted 2-phenyl-benzimidazole of the general formula I



wherein

R represents hydrogen or a metal cation, each of the symbols X and X₁ represents fluorine, chlorine or bromine, a trifluoromethyl group, an alkyl or alkoxy radical, a nitro, hydroxyl or amino group, an alkanoylamino group, a substituted or unsubstituted phenoxy or phenylsulphonyl group or the radical of a sulphonic acid or its amide or ester forms,

n represents a whole number from 1 to 4, and

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8. Agent according to claim 7, characterised in that it contains the active substances of formula I in finely distributed form and in admixture with suitable solid or liquid distributing agents, including surface active agents.



9. Process for the protection of keratin material from insects which injure such material, including their larvae, characterised by treating the keratin material with agents
5 which contain, as insecticidal active substances, substituted 2-phenyl-benzimidazoles of the general formula I given in claim 1.
10. Keratin material protected from injurious insects by the use of compounds of the general formula I given in claim 1.
11. Keratin material protected from injurious insects by the use of agents as claimed in claim 7.
- 15 12. Substituted 2-phenyl-benzimidazoles of the general formula I set forth in claim 1 wherein R, n and m have the meanings defined in claim 1 and X and X₁ have the meanings defined in claim 1 with the exception of the alkanoylamino group.
- 20 13. An insecticidal and acaricidal agent comprising as active ingredient a compound as claimed in claim 12.
- 25 14. Process for protecting keratin material from insects which injure the material which comprises treating the material with agents which contain an agent as claimed in claim 13.
15. Keratinous material whenever treated with an agent as claimed in claim 13.
16. Compounds as claimed in claim 12
30 as hereinbefore described in any one of the Examples 1 to 4.
17. Compounds as claimed in claim 1 as hereinbefore described in any of the Examples 1 to 4.
35
18. A process as claimed in claim 14 substantially as hereinbefore described in either of the Examples I and II.
19. A process as claimed in claim 9 substantially as hereinbefore described in either
40 of the Examples I and II.
20. An agent as claimed in claim 13 substantially as hereinbefore described in either of the Examples I and II.
21. An agent as claimed in claim 7 substantially
45 as hereinbefore described in either of the Examples I and II.
- W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.