

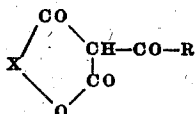
UNITED STATES PATENT OFFICE

2,127,879

TEXTILE OR THE LIKE PESTPROOFING
MEDIUM AND USEHenry Martin, Basel, Switzerland, assignor to
the firm of J. R. Geigy S. A., Basel, Switzer-
landNo Drawing. Application January 29, 1937, Se-
rial No. 123,061. In Germany February 7,
1936

11 Claims. (Cl. 167—37)

It has been found that compounds which con-
tain the five or six sided atomic ring group



in the molecule are valuable insect combatting
agents.

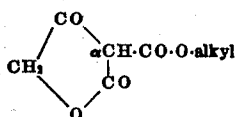
In the above formula:

X represents a single or double membered, satu-
rated or unsaturated, unsubstituted or sub-
stituted carbon bridge which closes the ring
and can at the same time be a member of
further ring systems, and

R represents —O-alkyl, —O-aralkyl, —NH₂,
—NH-alkyl, —NH-aryl, NH— and N=cyclo-
alkyl or corresponding single or mixed sub-
stituted tertiary amino groups, ureido- and
guanyl radicals, other nitrogen-containing
radicals or ring systems, or simple or substi-
tuted alkyl-, aralkyl- or aryl groups.

Such compounds are for example:

(1) Tetronic- α -carboxylic acid ester



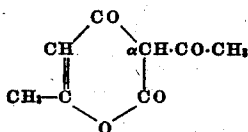
wherein alkyl is represented by the groups CH₃,
C₂H₅, C₃H₇, C₄H₉, C₆H₁₁. In the place of



in the above formula there can be the grouping

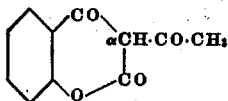


(2) Dehydracetic acid



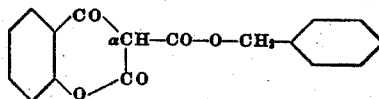
The two methyl groups can also be replaced by
one or two phenyl groups.

(3) α -Aceto-benzotetronic acid



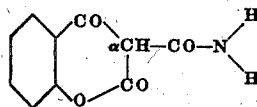
Instead of CH₃ other alkyl or aralkyl and aryl
groups such as ethyl, butyl, amyl, benzyl, phenyl-
ethyl, phenyl, p-chlorophenyl may be present.

(4) Benzotetronic acid- α -carboxylic acid-ben-
zylester

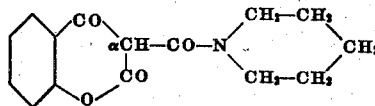


The chlorobenzyl, phenylethyl or alkyl radicals
from CH₃ to C₆H₁₁ may also replace the benzyl
group.

(5) Benzotetronic acid- α -carboxylic acid-amide

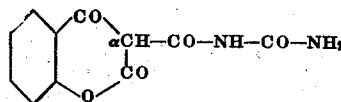


or the CH₃, C₂H₅, C₃H₇, C₄H₉, C₆H₁₁ amide thereof
(6) Benzotetronic acid- α -carboxylic acid-pi-
peridine

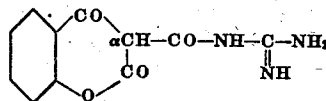


The nitrogen atom may bear other divalent cyclo-
alkyl radicals, nicotine or anabasine being em-
ployed in the place of piperidine.

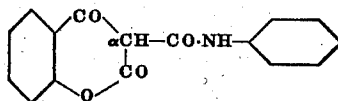
(7) Benzotetronic acid- α -carboxylic acid-ure-
ide



(8) Benzotetronic acid- α -carboxylic acid-
guanidide



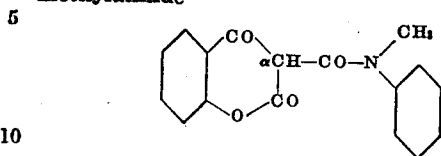
(9) Benzotetronic acid- α -carboxylic acid-anilide



Instead of the phenyl radical there may be men-
tioned tolyl, unsubstituted or substituted amino-
phenyl, mono- or dichloro-phenyl, α -/ β -naphthyl,

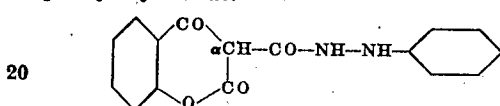
cyclohexyl, methyl-cyclohexyl, diethylaminoethylene and similar radicals.

(10) Benzotetronic acid- α -carboxylic acid-methylanilide



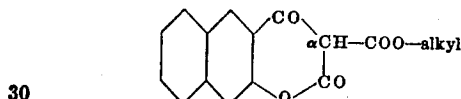
The alkyl group may vary from CH₃ to C₅H₁₁; instead of the phenyl radical there may be at the same place the groups mentioned below of Formula 9.

(11) Benzotetronic acid- α -carboxylic acid phenyl-hydrazide.

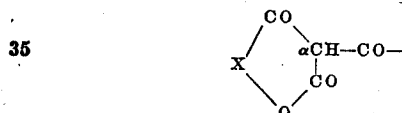


The phenylradical may also be substituted by one or more halogen atoms.

(12) 2,3-naphthotetronic acid- α -carboxylic acid-ester



The alkyl group may vary from CH₃ to C₅H₁₁. The atom grouping



is an essential part of all these compounds, X being a single or two membered carbon bridge. Through the substitution by three CO groups, the hydrogen atom of the α -carbon atom becomes very reactive, wherefore compounds of this kind have a strongly acid character. They therefore dissolve easily in alkalies and can be precipitated again by the addition of strong acids. By suitable substitution in the groups linked to the above typical atom grouping the solubility in water or organic solvents can be altered and the physiological effectiveness influenced. In particular amino or halogen substituents in the aromatic and aliphatic side groups have notable influence.

Substituted condensation products of unsaturated aromatic hydroxy-acids have already been proposed as insect destroying agents. Under these fall halogen substitution products of coumarin or the homologues thereof or the derivatives thereof, all substances containing a substituted pyrone ring. Fluoro-, bromo-, chloro-, alkyl, aryl- and thio-cumarines are named. The type of compound used in the present process can be termed an α -keto- γ -lacton, in which however to obtain remarkable effectiveness an additional -CO-group must be bound to the α -position carbon atom. Chemical consideration of the structure of these curamine derivatives in comparison with the present α -ketotetronic acids (α -carbonyltetronic acids) immediately shows the fundamental difference between them. Dehydracetic acid which is outstandingly effective, behaves chemically entirely differently from a coumarin. The same applies to the α -ketosubstituted tetronic acids.

Compared with the coumarin derivatives mentioned above, they are in part notably more ef-

fective and in part more bearable to the human skin (according to Anschütz, Annalen der Chemie, 1909, 367, page 201, halogen coumarines produce blisters on the skin and strong itching); in addition they are quite colourless, which is an advantage over the yellow coloured thiocoumarin; the latter feature is particularly important as regards the use of these insect combatting agents on textiles.

The above mentioned insect combatting agents can be employed by the usual processes. Solutions in water or in cheap organic solvents can be used for spreading, sprinkling or dipping the materials and textiles to be protected; they can also be atomized without harmful effects being noticed on warm-blooded beings. Pelts, feathers or wool treated with such solutions can be protected in a lasting manner against moths. Precipitation of the effective substance from alkaline solution on to the article to be protected by means of acid leads to the same result. If plant parasites are sprayed it will be found, for example on flies or walking-sticks that the poisoning effect by contact is very good.

Furthermore, solutions or emulsions in oils, creams, fats may be used or the compounds may be added to powders or they may be used in any form usual for combatting insects.

The following examples illustrate the invention, the parts being by weight:

Example I

2 parts of dehydracetic acid are dissolved in 98 parts of alcohol; pelts, feathers or wool are treated for example by dipping, then centrifuged and dried. The goods so treated are moth proof. Quite dilute solutions suffice to obtain a satisfactory protection against moths.

If instead of the above mentioned dehydracetic acid, use be made of derivatives of tetronic acids, such as dichlorbenzo- or benzotetronic acid-carboxylic acid ester, for example the methyl-, ethyl-, propyl-, amyl- and other esters, or other mentioned α -ketosubstituted tetronic acid derivatives such as ketones, carboxylic acid-amides, -anilides or -diethylethylenediamides, an equivalent effect is obtained.

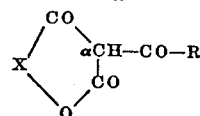
Certain parasites such as walking-sticks are killed by spraying with the above mentioned alcoholic solutions. The said compounds are also good when used as contact agents against flies.

Example II

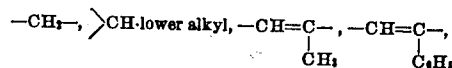
A concentrated aqueous solution of the compounds mentioned in Example I, is made with the aid of alkalies, the material to be treated dipped therein and then acidified, whereby a satisfactory protection against insects is again obtained.

What I claim is:

1. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



X being a ring closing grouping selected from the groups

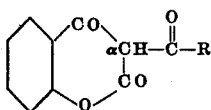


phenylene, naphthylene, and R being a mem-

ber of the group consisting of —O.lower alkyl, —O.aralkyl, —NH₂, —NH.lower alkyl, —NH.aryl, aryl.N.lower alkyl, —NH— and —N=cycloalkyl,

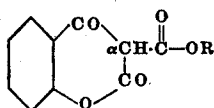
lower alkyl, aralkyl and phenyl.

2. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



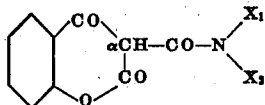
R being a member of the group consisting of —O.lower alkyl, —O.aralkyl, —NH₂, —NH.lower alkyl, —NH.aryl, aryl.N.lower alkyl, —NH— and —N=cycloalkyl, lower alkyl, aralkyl and phenyl.

3. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



R being a member of the group consisting of lower alkyl and aralkyl.

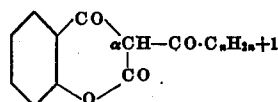
4. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



wherein X₁ is a member of the group consisting of H, lower alkyl, aryl of the benzene and naphthalene series, monovalent cycloalkyl radicals, and X₂ is a member of the group consisting of H, lower alkyl, aryl of the benzene series, X₁ and X₂ being together a divalent cycloalkyl radical.

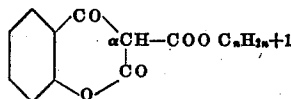
5. A devitalizing composition of matter for combatting pests of the insect class, containing

as its essential active ingredient a compound represented by the formula



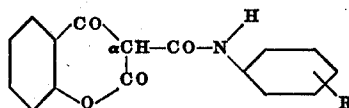
n being a number from 1 to 5.

6. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



n being a number from 1 to 5.

7. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient a compound represented by the formula



R being a member of the group consisting of zero and CH₃.

8. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient α-aceto-benzotetronic acid.

9. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient α-carbanilido-benzotetronic acid.

10. A devitalizing composition of matter for combatting pests of the insect class, containing as its essential active ingredient benzotetronic acid ethyl ester.

11. A method of protecting materials against pests of the insect class, comprising treating the materials first with a strong alkaline aqueous solution of a compound named in claim 1 and thereupon with an acid agent.

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