

Cl. 167

# ALIEN PROPERTY CUSTODIAN

## PREPARATIONS FOR PROTECTION FROM INSECTS

Eduard Dörr and Erich Goth, Wuppertal-Eibfeld, Germany; vested in the Alien Property Custodian

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This invention relates to materials for repelling insects, more particularly it relates to a combination of materials displaying in themselves a certain insect-repelling action with water-soluble alkaline-earth metal salts.

The use of various organic substances especially substances having a strong odor for warding off insects is known. The efficacy of these substances, however, is rather unsatisfactory and in particular does not last long. This disadvantage is, for instance, to be observed with coumarine and its substitution products.

In accordance with the present invention such organic substances which already have a certain insect repelling action and more particularly coumarine and its substitution products are combined with water-soluble alkaline-earth metal salts whereby the insect-repellent action is remarkably prolonged.

Substitution products of coumarine are for instance those deriving from coumarine substituted either in the benzene or in the pyrone ring system. Such substituents for instance halogen atoms including fluorine atoms and alkyl and aryl groups such as the ethyl- or methyl-group may for instance stand in 3- or 4-position. The same substituents as well as for instance hydroxyl groups which may be esterified or etherified may be present in the benzene nucleus, particularly in the 6- and/or 7-position. The CO-group of the pyrone ring system may be replaced by the CS-group.

Suitable insect repelling compounds in the preparations according to our invention are besides coumarine for instance 3-methyl-coumarine, 3-ethyl-coumarine, 4-methyl-coumarine, 4-ethyl- or isopropyl-coumarine, 4-bromo-, chloro- or fluoro-coumarine as well as 3-chloro-, 3-phenyl- or 4-phenyl-coumarine. Also derivatives of para-hydroxy-ortho-coumaric acid such as umbelliferone or  $\beta$ -methylumbelliferone may be advantageously used. Suitable substitution products of coumarine are for instance disclosed in U. S. Patent No. 1,995,247 to Berthold Günther Haring.

As watersoluble salts of the alkaline-earth metals, for instance halogenides, rhodanides, nitrates come into consideration. Suitable compounds are for instance strontium bromide, calcium chloride, calcium bromide, magnesium sulfate, magnesium chloride and calcium rhodanide. Of course, only those watersoluble salts of the alkaline-earth metals can be used which are innocuous to the human organism, especially the human skin.

The quantity and nature of the single constituents of our preparations may be varied within wide limits. They are preferably employed in suitable admixture, for instance, with the addition of extending agents, such as solvents or diluents emulsifying, dispersing or thickening agents, so that the preparation may be used in the form of a solution, emulsion, paste or powder. As extending agents the following substances may be mentioned by way of example: ethyl alcohol, aqueous ethyl alcohol, isopropanol, octodecyl alcohol, glycerine, kieselgur, talcum, plaster of Paris, paraffin, woolfat and other ointment bases such as eucerine, petroleum jelly, wax and starch. Further perfuming agents and cosmetic agents may be added.

For commercial reasons we generally prefer using coumarine, as the insect repellent constituent of our preparations; as watersoluble alkaline-earth metal salts the halogenides particularly the bromides and chlorides are used. As extender advantageously an aliphatic alcohol such as ethyl alcohol or octodecyl alcohol is present. The total amount of water in our preparations should preferably not substantially exceed 15%.

The invention is further illustrated by the following examples without, however, being restricted thereto, the parts being by weight:

### Example 1

	Parts
Coumarine .....	10
Calcium chloride .....	10
96% alcohol .....	80

yield a solution for warding off insects.

### Example 2

	Parts
Clove oil .....	5
Coumarine .....	3
Strontium bromide .....	8
Calcium chloride .....	6
85% alcohol .....	78

yield a solution for warding off insects.

### Example 3

	Parts
Coumarine .....	9
Calcium chloride .....	5.4
Magnesium chloride .....	1.7
96% alcohol .....	75
Water .....	9

yield a solution for warding off insects.

*Example 4*

	Parts
96% alcohol.....	15
Octodecyl alcohol.....	15
Coumarine.....	5
Calcium chloride.....	5

are melted together on the water bath while stirring and rapidly cooled. In this manner a paste is obtained which on application is suitable for warding off insects.

*Example 5*

	Parts
Coumarine.....	10
Calcium thiocyanate.....	6.8
96% alcohol.....	90

Instead of calcium thiocyanate for instance calcium nitrate or magnesium chloride may be used in equimolar amounts.

*Example 6*

	Parts
Coumarine fluoride.....	10
Calcium chloride.....	6
Magnesium chloride.....	4
Water.....	8
96% alcohol.....	85

*Example 7*

	Parts
3-phenyl coumarine.....	2
Calcium chloride.....	1
96% alcohol.....	234

*Example 8*

	Parts
Umbelliferone.....	2
Calcium chloride.....	1.38
96% alcohol.....	27

*Example 9*

	Parts
$\beta$ -methylumbelliferone.....	2
Calcium chloride.....	1.25
96% alcohol.....	54

*Example 10*

	Parts
4-methyl coumarine.....	15
Calcium chloride.....	11
96% alcohol.....	135

As compared with preparations containing no watersoluble alkaline-earth metal salts preparations of the kind specified exhibit a much more prolonged action in warding off insects. The increased efficacy of these preparations as compared with preparations containing no watersoluble alkaline-earth metal salts in most cases amounts to the two- or three-fold or even much higher value. This surprising increase of the efficacy is most likely due to the formation of double compounds between the organic active compounds and the alkaline-earth metals salts in the preparation.

This increase of the efficacy is illustrated by the following results of comparative tests:—

A preparation consisting of 10 parts of fluorocoumarine and 90 parts of a 96 per cent alcohol displays a sufficient insect repellent action still after 3 hours. Already after about 5 hours and a half the insect repellent action has disappeared. When using the preparation according to example 6 a sufficient insect repellent action is still observed after 9 hours.

A preparation consisting of 2 parts of phenyl coumarine and 234 parts of 96 per cent alcohol has lost its insect repellent action after 1 hour. To the contrary the preparation described in example 7 has preserved its full action still after 4 hours and even after 7 hours still displays a pronounced insect repellent action.

The tests were performed by putting an arm covered with the insect repellent preparation to be investigated into a small cage in which 1000-1500 mosquitos were kept. If within 5 minutes no mosquitos stung the insect repellent action of the preparation was regarded as being sufficient. If within this time more than 5 mosquitos stung the preparation was considered to be effectless.

This application is a continuation-in-part of our co-pending application Serial No. 119,364, filed January 6, 1937.

EDUARD DÖRR.  
ERICH GOTH.