

## PATENT SPECIFICATION

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## (54) CHEMICAL COMPOSITION AND PROCESS FOR ITS MANUFACTURE

(71) We, VELSICOL CHEMICAL CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 341 East Ohio Street, Chicago, Cook County, State of Illinois, 60611, United States of America, (assignee of DELBERT L. HANNA (deceased), and ALEXIS J. RUDNITSKI), 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 new composition consisting substantially of alpha-chlordane and beta-chlordane and substantially free of heptachlor. This invention further relates to a new process for preparing the afore-described composition.

For many years chlordane has played an important role as a commercial insecticide. It has been particularly valuable in the control of household pests, such as termites. Yet commercial chlordane has equal value as an agricultural insecticide.

Unfortunately, commercial chlordane is a mixture of many compounds. One of its important components is heptachlor. While heptachlor is also a commercial insecticide with important markets and is in fact a more efficacious insecticide than chlordane, its use does

present certain problems. In particular heptachlor and its metabolites are extremely persistent. Their long life has been deemed by many authorities as undesirable. Consequently, the use of heptachlor or products containing it are being restricted by governmental agencies. Furthermore, nonachlor also present in commercial chlordane, is a persistent insecticide confronted with ever increasing governmental restriction.

It has now been found that new compositions consisting substantially of alpha-chlordane and beta-chlordane are highly effective insecticidal products without the presence therein of substantial amounts of heptachlor 1, 4, 5, 6, 7, 8, 8-heptachloro-3a, 4, 7, 7a-tetrahydro 4, 7 methanoindene or nonachlor 1, 2, 3, 4, 5, 6, 7, 8, 8-nonachloro-3a, 4, 7, 7a-tetrahydro-4,7-methanoindene. While the latter two insecticides can be present in small amounts, in accordance with the present invention they are present in a combined total of less than 5% by weight of the composition, preferably about 2% by weight of the composition.

The prior literature has reported certain isomers of chlordane using several different systems of nomenclature. In order that there will not be ambiguity or confusion as to the present compositions, the following table relates the various nomenclature of the literature for the identical chlordane isomers:

| FAO/WHO <sup>1</sup> | BUCHEL <sup>2</sup> | COCHRANE <sup>3</sup> |
|----------------------|---------------------|-----------------------|
| alpha-chlordane      | beta-chlordane      | cis-chlordane         |
| gamma-chlordane      | alpha-chlordane     | trans-chlordane       |

<sup>1</sup>The Joint Expert Meeting of FAO/WHO Pesticide Residue Experts and CODEX Committee on Pesticide Residues.

<sup>2</sup>Buchel, H. H., Ginsberg, A. E. and Fischer, R. Chem. Ber., 99, 421 (1966).

<sup>3</sup>Chau, A. S. Y. and Cochrane, W. P., J. Ass. Offic. Anal. Chem. 52, 1092 (1969).

[Price 25p]

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11 In order to be consistent and unambiguous  
the nomenclature of Buchel will be used ex-  
clusively herein. For further purpose of identi-  
fication, alpha-chlordane has a melting point  
range of about 103°C—104°C and an infra-  
red absorption spectrum (CS<sub>2</sub> soln, 0.25 gms/  
5 ml) having identifying bands at 7.60, 7.98,  
8.20, 8.52, 9.17, 9.30, 9.73, 10.21, 11.10,  
12.12, 12.75, 13.33, and 14.25 microns. Beta-  
chlordane has a melting point range of about  
107—108°C and an infrared absorption spec-  
trum (CS<sub>2</sub> soln, 0.25 gms/5 ml) having identi-  
fying bands at 7.88, 8.57, 9.23, 9.30, 9.75,  
10.21, 11.10, 12.10, 13.27, 13.80, and 14.25  
microns. It can be seen that alpha-chlordane  
has an infrared absorption band 12.75 microns  
not found for beta-chlordane whereas beta-  
chlordane has an infrared absorption band at  
13.80 microns not found for alpha-chlordane.  
Each of these compounds has the empirical  
formula: C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>.

The new compositions of the present inven-  
tion consist substantially of alpha- and beta-  
chlordane. While each of these isomers have  
been individually reported in the literature,  
there is not previously disclosed compositions  
consisting substantially of these isomeric com-  
pounds and not containing more than minor  
amounts of less desired related products. One  
reason for this has been the absence of an  
acceptable process whereby such mixtures can  
be directly produced.

In particular the present compositions pre-  
ferably contain a minimum of 95% by weight  
of the alpha- and beta isomers. By this it can  
be seen that the related compounds, i.e., hepta-  
chlor and nonachlor, are present in small  
amounts. It is desirable that the content of the  
heptachlor and the nonachlor be as low as  
possible, since these two compounds have been  
declared by various governmental agencies not  
to be acceptable for certain insecticidal  
functions. Consequently, the present composi-

tions have utility not available for chlordane  
containing significant amounts of heptachlor  
and nonachlor. The amount of heptachlor pre-  
sent in the compositions of the invention is pre-  
ferably less than 3% and more preferably less  
than 1%.

While the ratio of the two chlordane isomers  
can vary depending on various factors includ-  
ing the desired insecticidal function, type of  
application, etc., the present invention con-  
templates that the weight ratio of alpha-chlor-  
dane to beta chlordane be between 1:1 and  
1:10. In such ratios maximum insecticidal prop-  
erties as well as the ease of formulating the  
product for its ultimate use are at a maximum.  
For certain applications it is preferred that the  
ratio of alpha-chlordane to beta-chlordane be  
between about 1:1 and 1:3. The present com-  
position contemplates that the content of com-  
pounds other than alpha- and beta-chlordane  
preferably be less than 5% by weight, and  
more preferably less than 1.0% by weight.

The efficiency of the present compositions  
as insecticides can be seen from the following  
insecticidal test data:—

In order to demonstrate the efficiency of  
the new compositions of the present invention,  
tests were performed using adult male German  
cockroaches (Susceptible WARR strain) as the  
test species. The test material of the present  
invention was formulated at a concentration  
of 25 mg/ml of a solution consisting of 481  
mg of emulsifier per ml of acetone. This solu-  
tion was diluted with tap water to the desired  
concentrations. For comparative purposes pre-  
sently commercial chlordane was similarly  
tested. Approximately six inch square plates  
were air dried for 24 hours after spraying  
and ten adult male German cockroaches were  
then exposed upon the treated surface for 30  
minutes. Observations were made 48 hours  
later, as follows:

Percent Control (Average of three tests)

| Conc. (ppm) | Present Product | Commercial<br>Chlordane |
|-------------|-----------------|-------------------------|
| 0.25        | 6               | 12                      |
| 0.50        | 37              | 9                       |
| 1.00        | 100             | 53                      |
| 2.00        | 100             | 88                      |

For practical use as insecticides, the com-  
pounds of this invention are generally incorpor-  
ated into insecticidal compositions which com-  
prise an inert carrier and an insecticidally toxic  
amount of such a compound. Such insecticidal

compositions, which can also be called formu-  
lations, enable the active compound to be  
applied conveniently to the site of the insect  
infestation in any desired quantity. These  
compositions can be solids, such as dusts,

granules or wettable powders; or they can be liquids such as solutions, aerosols or emulsifiable concentrates.

For example, dusts can be prepared by grinding and blending the active compound with a solid inert carrier such as the talcs, clays, silicas, pyrophyllite, and the like. Granular formulations can be prepared by impregnating the compound, usually dissolved in a suitable solvent, onto and into granulated carriers such as the attapulgites or the vermiculites, usually of a particle size range of from about 0.3 to 1.5 mm. Wettable powders, which can be dispersed in water and/or oil to any desired concentration of the active compound, can be prepared by incorporating wetting agents into concentrated dust compositions.

In some cases the active compounds are sufficiently soluble in common organic solvents such as kerosene or xylene so that they can be used directly as solutions in these solvents. Frequently, solutions of insecticides can be dispersed under superatmospheric pressure as aerosols. However, preferred liquid insecticidal compositions are emulsifiable concentrates, which comprise an active compound according to this invention and as the inert carrier, a solvent and an emulsifier. Such emulsifiable concentrates can be extended with water and/or oil to any desired concentration of active compound for application as sprays to the site of the insect infestation. The emulsifiers most commonly used in these concentrates are nonionic or mixtures of nonionic with anionic surface-active agents.

The dust ingredients are mixed in a mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the insect infestation.

The compositions of this invention can be applied as insecticides in any manner recognized by the art. The present invention therefore also provides a process for combating insects which comprises contacting insects with a composition of the invention or an insecticidal formulation of the invention. One method for destroying insects comprises applying to the locus of the insect infestation, an insecticidal composition comprising an inert carrier and, as the essential active ingredient, in a quantity which is toxic to said insects, the composition of the present invention. The concentration of the new compositions of this invention in the insecticidal compositions will vary greatly with the type of formulation and the purpose for which it is designed, but generally the insecticidal compositions will comprise from 0.05 to 95 percent by weight of the active components of this invention. In a preferred embodiment of this invention, the insecticidal compositions will comprise from 5 to 75 percent by weight of the active components. The compositions can also comprise such

additional substances as other pesticides, stabilizers, spreaders, deactivators, adhesives, stickers, fertilizers, activators, synergists, and the like.

The quantity of active compound of this invention to be used for insect control will depend on a variety of factors, such as the specific insect involved, intensity of the infestation, weather, type of environment, type of formulation, and the like. For example, the application of only one or two ounces of active chemical per acre may be adequate for control of a light infestation of an insect under conditions unfavorable for its feeding, while a pound or more of active compound per acre may be required for the control of a heavy infestation of insects under conditions favorable to their development.

The new process for the preparation of the afore-described compositions comprises the reaction of chlordene and chlorine in a solvent system containing carbon disulphide. Chlordene is a known compound readily prepared by the equimolar Diels-Alder adduction of cyclopentadiene and hexachlorocyclopentadiene, also described as 4,5,6,7,8-hexachloro-4,7-methano-3a,4,7,7a-tetrahydroindene.

This reaction can be performed at temperatures up to the reflux temperature of the reaction mixture. The reflux temperature will vary depending on the actual content of the reaction mixture. Thus while the reaction can be performed at temperatures up to the reflux temperature of the reaction mixtures, temperatures of between  $-20^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  are satisfactory, and temperatures between about  $5^{\circ}\text{C}$  and  $30^{\circ}\text{C}$  are preferred. While the present solvent system requires the presence of carbon disulphide it does not require that the solvent be exclusively carbon disulphide. While the use of solvent consisting exclusively of carbon disulphide does give the desired product containing negligible amount of heptachlor and nonachlor, it has been found that the carbon disulphide solvent can also contain up to 90% by weight carbon tetrachloride. This is particularly surprising since performing this reaction in solvent consisting exclusively of carbon tetrachloride will not produce the desired composition.

Since the present reaction involves the addition of one mole of chlorine to one mol. of chlordene, it is preferred that the chlorine and chlordene be present in this stoichiometric amount. By using less than the stoichiometric amount, the product will necessarily contain certain underchlorinated material and/or unreacted chlordene. The present process contemplates the use of at least about 0.9 mols of chlorine per mol. of chlordene. Since the reaction proceeds satisfactorily with equimolar amounts of chlordene and chlorine, there is no need for the use of excess chlorine. Although not preferred, excess chlorine can be used provided that the reaction is properly

followed by analysis of the reaction mixture so as to prevent excess reaction. If excess chlorine is permitted to react then undesired amounts of monoachlor are obtained. It is preferred that an excess of chlorine to be used be limited to 50% of the stoichiometric amount, preferably 10%.

The reaction is permitted to continue until analysis demonstrates that the product consists substantially of alpha and beta-chlordane. This can be done by convenient analytical procedures, such as infrared or gas chromatographic analysis. While reaction times of up to 3 hours can be used depending on the precise temperature and dilution of the reaction system, normally a reaction time of about 1 hour or less will suffice.

While the actual dilution of the reaction system is not material, it is preferred that all of the chlordene be in solution. The actual amount of solvent used will depend on the precise identity of the solvent. When the solvent consists of carbon disulphide, then at least about 1.27 pounds of carbon disulphide per pound of chlordene is used; when the solvent consists of 10% carbon tetrachloride and 90% carbon disulphide, then at least about 1.30 pounds per pound of chlordene is used.

The performance of the process does require the use of actinic light. Oxygen (air) interferes with the photocatalysis of chlorination reactions and should be excluded from the reaction medium. Other catalysts are not required.

Suitable materials of construction for commercial apparatus for conducting the process of this invention include glass and ceramics, nickel, Hastelloy C and Inconel (HASTELLOY and INCONEL are registered Trade Marks). Suitable sources of actinic light are mercury vapor lamps, electric light bulbs, fluorescent lamps, sunlight. Similarly, super-atmospheric pressure can be used but is not required for satisfactory performance.

The precise amount of solvent used is not material. Consequently, it is preferable to use sufficient solvent so that all of the chlordene is in solution. While the use of additional solvent may enhance the reaction, the advantages so obtained are minor; such excess dilution is inconvenient and is not preferred. Using a solvent consisting exclusively of carbon disulphide, the solubility of chlordene requires the presence of about 1.27 pounds of carbon disulphide per pound of chlordene reactant.

It has further been found possible to replace a portion of the carbon disulphide solvent with carbon tetrachloride. Since carbon tetrachloride is more easily handled than carbon disulphide, this has practical value. On the other hand, by using only carbon tetrachloride as solvent, the product can contain up to about 10% heptachlor. Since this is undesirable for many purposes the present process contemplates that the solvent system contain at least 10% carbon disulphide; preferably 25%; more preferably

50% and still more preferably 75%. The basis for this can be found in the following experimental test results.

The invention will now be further illustrated by reference to the following examples which are not intended to limit the scope of the invention:—

#### EXAMPLES 1—12.

Examples 1—7 were performed using identical equipment and procedures in order to demonstrate the effect of the present solvent system, including the effect of carbon tetrachloride as a component thereof. In each of these examples there was used as the reaction system 100 cc of a solution prepared by adding sufficient solvent to chlordene (5 lbs) so as to make one gallon of solution. This reaction solution was placed in a three-neck glass reaction flask equipped with stirrer, thermometer, chlorine inlet tube and vent. Two 15 watt blue fluorescent lamps were used as the light source. Chlorine was added intermittently in portions of about 1.6 grams, the reaction mixture being cooled to about 10°C before each addition of chlorine from the 30°C temperature caused by the chlorine addition. After removal of the solvent, the product was analyzed by gas chromatographic analysis.

Additional experiments were performed in order to further demonstrate the performance of the present process and the effect of variables such as the light source, solvent dilution, reaction temperature, etc., substantially using the foregoing procedures with the following variations:

In Example 8 the identical equipment as in Examples 1—7 was used except that an ultraviolet sun lamp was used as the light source. The solvent system consisted of 75% carbon disulphide, 25% carbon tetrachloride.

In Examples 9 through 12 the experiments were performed in a photochemical reaction vessel having a nominal capacity of 1000 cc. This device is supplied commercially by Ace Glass, Incorporated and is described on page 10 of their February 1969 Bulletin as being a reaction vessel constructed of borosilicate glass to accommodate an immersion well, and having an angled joint for sparger tube, one vertical joint for condenser, one threaded side arm to accommodate thermometer and a flat bottom to allow the use of stirrer bar if desired. The volume in the reactive area of the lamp is approximately 40—50% of total volume. This apparatus is equipped with a quartz lamp well which is surrounded by the reaction medium. About 1100 cc of solution was used in each experiment. The reactor was cooled by an ice bath. Chlorine was introduced through a Teflon "Teflon" is a registered Trade Mark) dip tube at the rate of about 3.3 grams/minute except for interruptions to sample the reaction mixture for analysis. The

reaction mixtures were sampled and analyzed by gas chromatography at approximately 90% of completion after which the stoichiometric amount of chlorine to complete the reaction was added, except in Example 11 an excess of chlorine was used.

In Example 9 the solvent system was 100% carbon disulphide and the reaction temperature was maintained between 20—30°C. One 15 watt blue fluorescent lamp was used in the lamp well as the light source.

In Example 10 the solvent system was 100% carbon disulphide. The light source was a 450 watt ultraviolet lamp. The reaction mixture dilution was 4.5 pounds of chlordene per gallon of solution. The reaction temperature was maintained between 20—30°C.

Example 11 was repeated as Example 12 except that the temperature was maintained between 9 and 15°C and excess chlorine was avoided.

The amounts of chlorine and chlordene used in Examples 9 to 12 were as follows:

| Example | Chlordene<br>(grams) | Chlorine<br>(grams) |
|---------|----------------------|---------------------|
| 9       | 675                  | 129                 |
| 10      | 600                  | 107                 |
| 11      | 300                  | more than 58        |
| 12      | 300                  | 58                  |

In all examples the reaction of chlordene and chlorine was performed in the absence of oxygen.

## RESULTS

| Example | Solvent Make-Up     |                        | Product Analysis |              |             |                   |                  |
|---------|---------------------|------------------------|------------------|--------------|-------------|-------------------|------------------|
|         | % Carbon disulphide | % Carbon tetrachloride | % Chlordene      | % Heptachlor | % Nonachlor | % Alpha-chlordane | % Beta-chlordane |
| 1       | 100                 | 0                      | NIL              | NIL          | 1.62        | 24.9              | 69.3             |
| 2       | 90                  | 10                     | NIL              | NIL          | NIL         | 25.5              | 68.2             |
| 3       | 75                  | 25                     | NIL              | NIL          | 0.44        | 25.5              | 69.0             |
| 4       | 75                  | 25                     | NIL              | NIL          | 0.58        | 27.0              | 69.5             |
| 5       | 50                  | 50                     | NIL              | 1.2          | 0.24        | 27.0              | 66.4             |
| 6       | 25                  | 75                     | NIL              | 2.4          | 0.37        | 28.4              | 63.6             |
| 7       | 90                  | 10                     | NIL              | NIL          | 0.59        | 25.5              | 68.2             |
| 8       | 75                  | 25                     | NIL              | NIL          | 1.51        | 27.0              | 69.5             |
| 9       | 100                 | 0                      | NIL              | 0.01         | 0.50        | 24.1              | 70.8             |
| 10      | 100                 | 0                      | NIL              | 0.2          | 0.20        | 23.7              | 68.6             |
| 11      | 100                 | 0                      | NIL              | 0.2          | 2.81        | 22.2              | 73.1             |
| 12      | 100                 | 0                      | NIL              | 0.1          | 0.44        | 23.0              | 72.8             |

## WHAT WE CLAIM IS:—

1. A composition consisting substantially of alpha-chlordane having a melting point range of about 103—104°C and an infrared absorption spectrum having (CS<sub>2</sub> solution, 0.25 gms/5 ml) identifying bands at 7.60, 7.98, 8.20, 8.52, 9.17, 9.30, 9.73, 10.21, 11.10, 12.12, 12.75, 13.33 and 14.25 microns and beta-chlordane having a melting point range of about 107—108°C and an infrared absorption spectrum (CS<sub>2</sub> soln, 0.25 gms/5 ml) having identifying bands at 7.88, 8.57, 9.23, 9.30, 9.75, 10.21, 11.10, 12.10, 13.27, 13.80 and 14.25 microns, the composition containing a total of less than 5% by weight of heptachlor and nonachlor.
2. A composition as claimed in claim 1 in which the weight ratio of the alpha-chlordane to beta-chlordane is between 1:1 and 1:10.
3. A composition as claimed in claim 2, in which the ratio of the alpha-chlordane to beta-chlordane is between 1:1 and 1:3.
4. A composition as claimed in any one of claims 1 to 3 in which the alpha and beta-chlordane constitute at least 95% by weight of the composition.
5. A composition as claimed in any one of the preceding claims which contains less than 3% by weight heptachlor.
6. A composition as claimed in claim 5 which contains less than 1% heptachlor.
7. An insecticidal formulation comprising a composition as claimed in any one of the preceding claims together with an inert carrier.
8. A formulation as claimed in claim 7 comprising from 0.05 to 95% by weight of a composition of any one of claims 1 to 6.
9. A formulation as claimed in claim 8, comprising from 5 to 75% by weight of a composition as claimed in any one of claims 1 to 6.
10. A formulation as claimed in any one of claims 7 to 9, which is in the form of a dust, granule, wettable powder, solution, aerosol or emulsifiable concentrate.
11. A process for the production of a composition as claimed in claim 1, which com-

prises reacting chlordene and chlorine in the presence of actinic light and in the absence of oxygen at a temperature up to the reflux temperature of the reaction mixture, in carbon disulphide solvent until there is formed a product consisting substantially of alpha and beta-chlordane.

12. A process as claimed in claim 11, in which the reaction is performed at a temperature of between -20°C and 40°C.

13. A process as claimed in claim 12, in which the reaction is performed at a temperature of between 5°C and 30°C.

14. A process as claimed in any one of claims 11 to 13 in which the solvent is a mixture of carbon disulphide and carbon tetrachloride containing at least 10% by weight carbon disulphide.

15. A process as claimed in claim 14, in which the solvent is a mixture of carbon disulphide and carbon tetrachloride containing at least 25% by weight carbon disulphide.

16. A process as claimed in claim 15 in which the solvent is a mixture of carbon disulphide and carbon tetrachloride containing at least 50% by weight carbon disulphide.

17. A process as claimed in any one of claims 11 to 13 in which the solvent is 100% carbon disulphide.

18. A method of combating insects which comprises contacting insects with a composition as claimed in any one of claims 1 to 6.

19. A method of combating insects which comprises contacting insects with a formulation as claimed in any one of claims 7 to 10.

20. A composition as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

21. A process as claimed in claim 11 substantially as hereinbefore described in any one of the Examples.

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