

1.076.139



# PATENT SPECIFICATION

NO DRAWINGS

1.076.139

Date of Application and filing Complete Specification: Dec. 9, 1964.

No. 50142/64.

Two Applications made in Japan (Nos. 67279, 67280) on Dec. 14, 1963.

Complete Specification Published: July 19, 1967.

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Index at acceptance:—A5 E(1C4A2, 1C4A3, 1C4A4)

Int. Cl.:—A 01 n 5/00

## COMPLETE SPECIFICATION

### Herbicidal Compositions

We, TOA GOSEI KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese Body Corporate of 2—8, Shiba-Tamuracho, Minato-ku, Tokyo, Japan, and IHARA CHEMICALS CO., LTD., a Japanese Body Corporate of 100, Shibukawa, Shimizu-shi, 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 herbicidal compositions.

3,4-dichloropropionanilide (DCPA) has been used in practice as a selective contact-type herbicide. Thus it will kill various weeds without injuring rice plant genera such as paddy field rice plant and upland rice plant.

DCPA is generally prepared as an emulsifiable concentrate, which before use is diluted to a concentration of 0.2—0.4% by weight with water and sprayed on the stems and leaves of the growing plant. When a conventional emulsifiable concentrate of DCPA is diluted to convert it into a form suitable for spraying, the DCPA often crystallizes out. Furthermore, even after spraying, needle crystals may sometimes separate out on the plant. When DCPA is used in a rainy season, such crystals are washed off the plant by the rain, thereby considerably reducing the herbicidal activity of the sprayed composition. As a result, the use of DCPA has been associated with uncertain herbicidal activity and phytotoxic spots sometimes occur on useful plants.

After numerous investigations on DCPA compositions, it has now been discovered that 2 - (1 - cyclohexenyl)cyclohexanone (CHCH), which is a stable liquid at room temperature and water-insoluble, is a good solvent for DCPA. Further, CHCH is capable of dissolving the outer wax-like substance of plant bodies and of penetrating rapidly into the plant. Furthermore, CHCH itself is herbicidally active and if an emulsifiable concentrate of CHCH is diluted and sprayed on the stems and leaves of plants, a herbicidal effect is

apparent with a concentration of CHCH of 0.2% by weight. With a concentration of CHCH of 1% by weight, weeds such as Barnyard grass (*Echinochloa crusgalli* P. Beauv) and Crabgrass (*Digitaria adscendens* Henr.) are completely killed. Characteristic of the herbicidal activity of CHCH is the rapidity with which a herbicidal effect can be obtained. For example, with a composition containing a suitable amount of CHCH, indications of damage to the weeds can be observed after only 30 minutes from spraying and, after 3 hours, the leaves droop and fade. However, although CHCH possesses such contact herbicidal properties, its use suffers from the disadvantages that it is less active than DCPA, necessitating the use of uneconomic amounts, and the safety range for plants (width of selective activity) is narrow.

The present invention provides herbicidal compositions comprising as active ingredients 3,4 - dichloropropionanilide and 2 - (1-cyclohexenyl) cyclohexanone. It will, of course, be appreciated that the term "herbicidal composition" includes concentrates that will be diluted before use.

By incorporating CHCH in the DCPA compositions in accordance with the invention, the crystallising-out of the DCPA referred to herebefore in dilute solution and on the plant after spraying can be prevented. Furthermore, the penetration of the DCPA into the plant body, and the rapidity of the herbicidal effect, can be substantially increased. Accordingly, the useful life of the compositions after spraying is less affected by rain.

Furthermore, the presence of the CHCH increases the degree to which the plants will absorb the compositions, which increases the herbicidal effect, particularly in cold weather or with plants which are in a cold position.

The relative proportions of CHCH and DCPA can be varied widely and suitable proportions for a particular application can readily be determined by routine experiment. Preferably, however, the composition contains at least

[Price 4s. 6d.]

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75

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85

90

necessitating

spots

- by 0.05 part by weight, e.g. 0.05—3 parts by weight, of CHCH for each 1 part of weight of DCPA. With a smaller proportion of CHCH, the DCPA may begin to crystallise out 2 days after spraying, which is not desirable.
- 5 With compositions containing 0.2 to 3 parts of CHCH per 1 part of DCPA, a considerable synergistic effect is observed in the herbicidal properties. Further, the CHCH dissolves the DCPA so thoroughly that, when a dilute solution is prepared, the DCPA does not crystallise out to any significant extent and, when sprayed on the plants, the compositions penetrate the plant body easily and rapidly and give rapid, specific herbicidal activity against the following weeds:
- 120 Barnyard grass (*Echinochloa Crus-galli* P. BEAUV.)  
 Crabgrass (*Digitaria adscendens* HENR.)  
 Goose-grass (*Eleusine indica* GAERTN.)  
 Green foxtail (*Setaria viridis* P. BEAUV.)  
 Green pigweed (*Chenopodium album* var. *centrorubrum* MAKINO)  
 Smart-weed (*Polygonum conspicuum* NAKAI)  
 French-weed (*Galinsoga parviflora* CAVANILLES)  
 Chickweed (*Stellaria media* CRY.)  
 Milk purslane (*Euphorbia supina* RAFIN.)  
 30 Cudweed (*Gnaphalium japonicum* THUMB.)  
 Rotala indica KOEHNE  
 Dopotrium junceum HAMILT  
 35 Water wort (*Elatine triandra* SCHK.)  
 Pickerel-weed (*Monochloria vaginalis* PRESL.)  
 Autumn rush (*Fimbristylis littoralis* GAUDICH.)  
 40 without harming rice plant genera. Such compositions show a 3—4 times larger herbicidal effect 2 days after spraying and a 2—3 times larger herbicidal effect after 10 days compared with the use of DCPA only.
- 45 The compositions of the invention may contain a "carrier", i.e. a solid or liquid diluent for the active ingredients.
- For example, the carrier may be a solvent for DCPA and CHCH, or a non-solvent for DCPA and CHCH in which the DCPA and CHCH can be homogeneously dispersed by means of additives such as surfactants. Examples of such carriers are water, liquid hydrocarbons such as benzene, kerosene, alcohols, acetone, methylnaphthalene and cyclohexanone, animal or vegetable oils, fatty acids and fatty acid esters.
- When carriers are used, the compositions should contain at least 0.1 weight percent of the active ingredients.
- 60 Furthermore, the compositions may desirably contain additives besides surfactants that are conventionally used in agricultural chemistry, e.g. spreaders, emulsifiers, wetting agents and adhesives, in order to make the herbicidal effect more positive.
- The following Examples further illustrate the invention.
- EXAMPLE 1
- 30 Thirty five grams of DCPA, 10 grams of cyclohexanone, 28 grams of methylnaphthalene, and 25 grams of the emulsifier made by Toho Kagaku Kogyo Co. and sold under the Registered Trade Mark "Sorpoal" were mixed and 2 grams of CHCH was added to the mixture. The resulting composition was diluted with 20 l. of water, and the solution was used as a spraying liquid.
- 75
- EXAMPLE 2
- 30 35 grams of DCPA, 10 grams of cyclohexanone, 25 grams of xylene and 25 grams of the emulsifier made by Takemoto Yushi Co. and sold under the Registered Trade Mark "Newcalgen" were mixed and 5 grams of CHCH was added to the mixture. The resulting composition was diluted with 20 l. of water, and the solution was used as a spraying liquid.
- 85
- EXAMPLE 3
- 30 35 grams of DCPA, 30 grams of xylene and 25 grams of the emulsifier "Sorpoal" were mixed and 10 grams of CHCH was added to the mixture. The resulting composition was diluted with 25 l. of water, and the solution was used as spraying liquid.
- 95
- EXAMPLE 4
- 30 35 grams of DCPA, 33 grams of xylene and 20 grams of the emulsifier "Sorpoal" were mixed and 12 grams of CHCH was added to the mixture. The resulting composition was diluted with 25 l. of water, and the solution was used as a spraying liquid.
- 100
- EXAMPLE 5
- 30 35 grams of DCPA, 10 grams of cyclohexanone, 12 grams xylene and 25 grams of the emulsifier "Newcalgen" were mixed and 18 grams of CHCH was added to the mixture. The resulting composition was diluted with 25 l. of water, and the solution was used as a spraying liquid.
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- EXAMPLE 6
- 30 35 grams of DCPA, 5 grams of xylene and 25 grams of the emulsifier "Sorpoal" were mixed and 35 grams of CHCH was added to the mixture. The resulting composition was diluted with 30 l. of water, and used as a spraying liquid.
- 115
- The activity and effect of the compositions of the invention are shown in the following experimental Examples. The sample liquids were prepared by diluting a mixture of 35 grams of DCPA, 50 grams of xylene and 15 grams of "Sorpoal", and a mixture of 50 grams of CHCH, 40 grams of xylene and 10
- 120

grams of "Sorpoo", with water and combining the diluted mixtures in appropriate amounts.

#### EXPERIMENTAL EXAMPLE 1

##### 5 Crystallization and decrease of phytotoxicity. a. Experiment

Paddy field rice plant seeds (Species Kinapu) were each seeded in a pot of diameter

12 cm and at the 5-leaf stage 20 cc. of each composition were sprayed onto the plants through a glass nozzle. The plants were then examined after 2 days and after 10 days from spraying. The "crystallization number" is the number of crystals which have developed within 5 cm of the leaf blade (central portion) in needle state and averaged over three leaves.

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##### b. Results

| Exp. No. | Compound     | Concentration<br>% by wt. | Crystallization<br>number | Phytotoxicity for<br>paddy field rice plant<br>(5-leaf stage) |                              |
|----------|--------------|---------------------------|---------------------------|---------------------------------------------------------------|------------------------------|
|          |              |                           | 2 days after<br>treating  | 2 days<br>after<br>treating                                   | 10 days<br>after<br>treating |
| 1        | DCPA         | 0.2                       | 54.3                      | —                                                             | —                            |
| 2        | DCPA<br>CHCH | 0.2<br>0.1                | 0                         | —                                                             | —                            |
| 3        | DCPA<br>CHCH | 0.2<br>0.05               | 0                         | —                                                             | —                            |
| 4        | DCPA<br>CHCH | 0.2<br>0.02               | 0                         | —                                                             | —                            |
| 5        | DCPA<br>CHCH | 0.2<br>0.01               | 8.2                       | —                                                             | ±                            |
| 6        | Water        |                           | —                         | —                                                             | —                            |

Exp. Nos. 2—5 are with compositions according to the invention.

Exp. Nos. 1 and 6 are comparative examples.

—: Represents no significant harm to the plants.

±: Represents very little significant harm to the plants.

#### EXPERIMENTAL EXAMPLE 2

##### 20 The effect of rain in the contact treatment of Barnyard grass (*Echinochloa Crus-galli* P. Beauv.) with DCPA/CHCH mixtures.

##### a. Experiment

25 15 Barnyard grass (*Echinochloa Crus-galli*  
P. Beauv.) weeds (2-leaf stage) previously  
seeded in small pots were selected and 1, 3, 6  
and 24 hours after spraying with 3 ml. of  
liquid of the indicated concentrations using a  
glass nozzle, 5 mm and 10 mm of artificial rain

were applied to different sets of weeds and the effects of the compositions were determined to check the influence of the rain. The artificial rain was produced by raining 5 mm (450 c.c.) and 10 (900 c.c.) on vats having a definite area (900 cm<sup>2</sup>) by means of ladle type sprayer so that the weeds spent 15 minutes in the 5 mm of artificial rain and 30 minutes in the 10 mm. The determinations were carried out one week after the treatment.

30

mm

35 a

## b. Results

| Exp. No. | Compound     | *<br>**<br>*** | 0mm | 5mm |     |     |     | 10mm |     |     |     |
|----------|--------------|----------------|-----|-----|-----|-----|-----|------|-----|-----|-----|
|          |              |                | —   | 1   | 3   | 6   | 24  | 1    | 3   | 6   | 24  |
| 1        | DCPA         | 0.3            | 100 | 54  | 78  | 89  | 100 | 52   | 68  | 76  | 100 |
| 2        | „            | 0.2            | 100 | 30  | 52  | 74  | 89  | 26   | 45  | 58  | 80  |
| 3        | DCPA<br>CHCH | 0.2<br>0.1     | 100 | 100 | 100 | 100 | 100 | 100  | 100 | 100 | 100 |
| 4        | { „          | 0.2<br>0.05    | 100 | 100 | 100 | 100 | 100 | 92   | 100 | 100 | 100 |
| 5        | { „          | 0.2<br>0.02    | 100 | 96  | 100 | 100 | 100 | 80   | 98  | 100 | 100 |
| 6        | { „          | 0.2<br>0.01    | 100 | 85  | 100 | 100 | 100 | 76   | 83  | 100 | 100 |
| 7        | Non-treated  | —              | —   | —   | —   | —   | —   | —    | —   | —   | —   |

\*mark represents Amount of rain.

\*\*mark represents Hours before raining after spraying of the composition.

\*\*\*mark represents concentration (% by wt).

Exp. Nos. 3—6: The Compositions of the invention

Exp. Nos. 1, 2 and 7: Comparative examples

The numerals in the table show the kill ratio.

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$$\text{Kill ratio} = \frac{100 n_3 + 75 n_4 + 50 n_5 + 25 n_2}{N}$$

where

 $n_5$  = Number of leaves which are 100% killed $n_4$  = Number of leaves which are 75% killed $n_3$  = Number of leaves which are 50% killed $n_2$  = Number of leaves which are 25% killed $N$  = Total number of leaves

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## EXPERIMENTAL EXAMPLE 3

The herbicidal effect and phytotoxicity of DCPA/CHCH mixtures (I)

## 15 a. Experiment

In a wooden box of base area 800 cm<sup>2</sup> packed with upland soil were seeded 50 seeds each of paddy field rice (species, Kinnanpu) and Barnyard grass (*Echinochloa Crus-galli* P.

Beauv.) After germination, at 3-leaf stage (plant length of 7 cm), each box was treated with 10 mil. of liquid of the indicated concentration, the liquid being distributed uniformly over the soil. After one week the degrees of injury of the paddy field rice plant and Barnyard grass (*Echinochloa Crus-galli* P. Beauv.) were determined.

the

20

25

area

## b. Results

| Exp. No. | Compound       | Concentration | General condition of paddy field rice plant |                              |                         | Barnyard grass |       |
|----------|----------------|---------------|---------------------------------------------|------------------------------|-------------------------|----------------|-------|
|          |                |               | Number of sound leaves                      | Number of half killed leaves | Number of killed leaves | Killed         | Sound |
| 1        | DCPA           | 0.1           | 5                                           | 6                            | 1                       | 14             | 34    |
| 2        | "              | 0.2           | 5                                           | 4                            | 1                       | 27             | 18    |
| 3        | "              | 0.3           | 3                                           | 4                            | 2                       | 45             | 0     |
| 4        | CHCH           | 0.05          | 8                                           | 0                            | 0                       | 0              | 48    |
| 5        | "              | 0.2           | 8                                           | 0                            | 0                       | 9              | 41    |
| 6        | "              | 0.3           | 6                                           | 2                            | 0                       | 16             | 32    |
| 7        | "              | 0.5           | 5                                           | 4                            | 0                       | 28             | 23    |
| 8        | { DCPA<br>CHCH | 0.2<br>0.02   | —5                                          | 3                            | 2                       | 29             | 18    |
| 9        | { "            | 0.25<br>0.05  | 7                                           | 2                            | 0                       | 45             | 0     |
| 10       | { "            | 0.2<br>0.05   | 7                                           | 3                            | 0                       | 47             | 0     |
| 11       | { "            | 0.1<br>0.05   | 6                                           | 3                            | 0                       | 37             | 8     |
| 12       | { "            | 0.2<br>0.1    | 4                                           | 5                            | 2                       | 48             | 0     |
| 13       | { "            | 0.1<br>0.1    | 5                                           | 4                            | 1                       | 41             | 3     |
| 14       | { "            | 0.2<br>0.2    | 4                                           | 4                            | 1                       | 46             | 0     |
| 15       | { "            | 0.1<br>0.2    | 7                                           | 4                            | 1                       | 38             | 1     |
| 16       | { "            | 0.05<br>0.15  | 7                                           | 2                            | 0                       | 30             | 9     |
| 17       | { "            | 0.04<br>0.16  | 8                                           | 0                            | 0                       | 12             | 33    |
| 18       | { "            | 0.06<br>0.24  | 7                                           | 1                            | 0                       | 14             | 32    |
| 19       | Non-treated    | —             | 14                                          | 0                            | 0                       | 0              | 45    |

Exp. Nos. 8—18: The compositions of the invention.

Exp. Nos. 1—7 and 19: Comparative examples.

## EXPERIMENTAL EXAMPLE 4

a. The herbicidal effect and phytotoxicity of DCPA/CHCH mixtures (II)

5 Seeds of paddy field rice plant and Crabgrass (*Digitaria adscendens* HENR.) were seeded in pots and, when they reached the 2-

leaf stage, the total surfaces of the leaves were treated with liquid of the indicated concentrations. 2 days and 10 days after the treatment the conditions of the plant and grass were determined. 10

## b. Results

| Exp. No. | Compound     | Concentration | Kill ratio for Crabgrass |               | Kill ratio for paddy field rice plant |               |
|----------|--------------|---------------|--------------------------|---------------|---------------------------------------|---------------|
|          |              |               | After 2 days             | After 10 days | After 2 days                          | After 10 days |
| 1        | DCPA         | 0.3           | 100                      | 100           | 11                                    | 23            |
| 2        | "            | 0.2           | 74—50                    | 100           | 0                                     | 0             |
| 3        | "            | 0.15          | 48                       | 52—78         | 0                                     | 0             |
| 4        | "            | 0.1           | 24                       | 28—53         | 0                                     | 0             |
| 5        | CHCH         | 0.3           | 26—53                    | 54            | 0                                     | 0             |
| 6        | "            | 0.2           | 9                        | 11            | 0                                     | 0             |
| 7        | "            | 0.15          | 0                        | 0             | 0                                     | 0             |
| 8        | "            | 0.07          | 0                        | 0             | 0                                     | 0             |
| 9        | DCPA<br>CHCH | 0.15<br>0.15  | 100—78                   | 100           | 0                                     | 0             |
| 10       | "            | 0.15<br>0.1   | 100—76                   | 100           | 0                                     | 0             |
| 11       | "            | 0.15<br>0.07  | 78                       | 100           | 0                                     | 0             |
| 12       | "            | 0.1<br>0.1    | 79                       | 100           | 0                                     | 0             |
| 13       | "            | 0.1<br>0.07   | 75                       | 100—78        | 0                                     | 0             |
| 14       | "            | 0.1<br>0.05   | 72—51                    | 100—75        | 0                                     | 0             |
| 15       | Non-treated  | —             | —                        | —             | —                                     | —             |

Exp. Nos. 9—14: The compositions of the invention

Exp. Nos. 1—8 and 15: Comparative examples

The numerals in the table show the kill ratio which is as defined in Experimental Example No. 2.

## WHAT WE CLAIM IS:—

15 1. Herbicidal compositions comprising as active ingredients 3,4-dichloropropionanilide and 2-(1-cyclohexenyl) cyclohexanone.

20 2. Herbicidal compositions according to claim 1 containing 0.2 to 3 parts by weight of 2-(1-cyclohexenyl) cyclohexanone for each 1 part by weight of 3,4-dichloropropionanilide.

3. Herbicidal compositions according to claim 1 containing 0.05 to 0.2 part by weight of 2-(1-cyclohexenyl) cyclohexanone for each 1 part by weight of 3,4-dichloropropionanilide.

25 4. Herbicidal compositions according to claim 1, 2 or 3 which contain at least 0.1 weight percent of the active ingredients in association with a carrier.

## EXPERIMENTAL EXAMPLE 4

a. The herbicidal effect and phytotoxicity of DCPA/CHCH mixtures (II)

5 Seeds of paddy field rice plant and Crabgrass (*Digitaria adscendens* HENR.) were seeded in pots and, when they reached the 2-

leaf stage, the total surfaces of the leaves were treated with liquid of the indicated concentrations. 2 days and 10 days after the treatment the conditions of the plant and grass were determined. 10

## b. Results

| Exp. No. | Compound     | Concentration | Kill ratio for Crabgrass |               | Kill ratio for paddy field rice plant |               |
|----------|--------------|---------------|--------------------------|---------------|---------------------------------------|---------------|
|          |              |               | After 2 days             | After 10 days | After 2 days                          | After 10 days |
| 1        | DCPA         | 0.3           | 100                      | 100           | 11                                    | 23            |
| 2        | "            | 0.2           | 74—50                    | 100           | 0                                     | 0             |
| 3        | "            | 0.15          | 48                       | 52—78         | 0                                     | 0             |
| 4        | "            | 0.1           | 24                       | 28—53         | 0                                     | 0             |
| 5        | CHCH         | 0.3           | 26—53                    | 54            | 0                                     | 0             |
| 6        | "            | 0.2           | 9                        | 11            | 0                                     | 0             |
| 7        | "            | 0.15          | 0                        | 0             | 0                                     | 0             |
| 8        | "            | 0.07          | 0                        | 0             | 0                                     | 0             |
| 9        | DCPA<br>CHCH | 0.15<br>0.15  | 100—78                   | 100           | 0                                     | 0             |
| 10       | "            | 0.15<br>0.1   | 100—76                   | 100           | 0                                     | 0             |
| 11       | "            | 0.15<br>0.07  | 78                       | 100           | 0                                     | 0             |
| 12       | "            | 0.1<br>0.1    | 79                       | 100           | 0                                     | 0             |
| 13       | "            | 0.1<br>0.07   | 75                       | 100—78        | 0                                     | 0             |
| 14       | "            | 0.1<br>0.05   | 72—51                    | 100—75        | 0                                     | 0             |
| 15       | Non-treated  | —             | —                        | —             | —                                     | —             |

Exp. Nos. 9—14: The compositions of the invention

Exp. Nos. 1—8 and 15: Comparative examples

The numerals in the table show the kill ratio which is as defined in Experimental Example No. 2.

## WHAT WE CLAIM IS:—

15 1. Herbicidal compositions comprising as active ingredients 3,4-dichloropropionanilide and 2-(1-cyclohexenyl) cyclohexanone.

20 2. Herbicidal compositions according to claim 1 containing 0.2 to 3 parts by weight of 2-(1-cyclohexenyl) cyclohexanone for each 1 part by weight of 3,4-dichloropropionanilide.

3. Herbicidal compositions according to claim 1 containing 0.05 to 0.2 part by weight of 2-(1-cyclohexenyl) cyclohexanone for each 1 part by weight of 3,4-dichloropropionanilide.

25 4. Herbicidal compositions according to claim 1, 2 or 3 which contain at least 0.1 weight percent of the active ingredients in association with a carrier.



\* C L M S \*

5. Herbicidal compositions according to any one of claims 1 to 5 where appropriate claim 1, substantially as described in the foregoing Examples. after dilution.

5 6. Method for inhibiting the growth of weeds J. A. KEMP & CO.,  
at a *locus*, which comprises applying to the Chartered Patent Agents,  
*locus* a herbicidal composition as claimed in 14, South Square, Gray's Inn, London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.  
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.



\* C L M S \*