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[54] Title: WATER-FLOATABLE AGGREGATIVE SOLID AGRICULTURAL PREPARATIONS

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[57] ABSTRACT

A water-floatable, aggregate solid agricultural preparation carrying a carbamate agricultural chemical as the active ingredient and an organic compound having a partition coefficient of said carbamate agricultural chemical to water of not less than 10^2, on a solid carrier.

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WATER-FLOATABLE, AGGREGATIVE SOLID AGRICULTURAL PREPARATIONS

ABSTRACT OF THE DISCLOSURE

A water-floatable, aggregative solid agricultural preparation carrying a carbamate agricultural chemical as the active ingredient and an organic compound having a partition coefficient of said carbamate agricultural chemical to water of not less than 10^2, on a solid carrier.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to water-floatable, aggregative solid agricultural preparations, especially those containing carbamate agricultural chemicals and specific organic compounds.

2. Description of the Prior Art

A research is now being tried regarding the granular preparations which were given a water-floatability by coating or absorbing an insecticidal or like component with a water-floatable carrier and coating the resultant with a water repellent, alternatively by granulating a mixture of an insecticidal or like component and a carrier and coating the granules with a water repellent.

For example, Japanese Patent Publication No. 48(1973)-15613 discloses a floatable granular preparation which was made by adsorbing an insecticidal component and a surfactant or water repellent on the base which was obtained by sticking and coating a submersible solid substance and a floatable substance together with a binder, and Japanese Patent Publication No. 47(1972)-1240 discloses a floatable preparation which binds an insecticidal component to a

calcined perlite together with a polybutane. Japanes Patent Publication No. 49(1974)-11421 discloses a granular preparation for paddy water application of an insecticidal compound which exerts an insecticidal effect by evaporating gas therefrom. This granular preparation is obtained by sticking fine powders, which are given water repellent properties by mixing a volatile insecticidal compound and a water repellent with or without a carrier, to the surface of a granular base.

Moreover, Japanese Patent Publication No. 44(1969)-8600 discloses a floatable granular insecticidal composition prepared by adsorbing an active component on granular pumice or vermiculite having 30-50% of water-absorbability as carrier and coating the resultant with a higher fatty acid.

However, all of the prior art references stated above require the use of the water-floatable carrier [Japanese Patent Publication Nos. 48(1973) - 15613 and 47(1972) - 1240] or the carrier of pumice or vermiculite having a specified water-absorbability [Japanese Patent Publication No. 44(1969) - 8600, or are limited to the granular preparations which utilize the volatile insecticidal component (Japanese Patent Publication No. 49(1974)-11421). Or, they show a drawback of not in practical use because said preparation have very complexed composition. Moreover, while these preparations have a merit to reduce

parts to be wasted because of adsorption by soil or dissolution to the bottom water due to their floatation when they are applied to paddy water as granular preparations, they have still disadvantages that some parts of them d o not well come into contact with plants and are wasted because the active component scatters to a whole water surface or is less adherency to plants.

The inventions of the present invention aimed to find an agricultural preparation that when it is subjected to paddy water application, an active ingredient can come into contact with a plant effectively and ascend the surface of stem due to the phenomenon of capillarity or stick directly to leaf and stem of plant, thereby giving a high control efficacy around the plant stock base region or plant foot.

SUMMARY OF THE INVENTION

Thus, the inventions have unexpectedly found that carbamate agricultural chemicals have a desirable spreadability on a water surface (hereinafter called as "spredability"). When this sprefadability of carbamate agricultural chemicals is utilized, it was also found that active ingredients including other insecticides or fungicides are simultaneously spread

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and aggregated or accumulated around water surface at a high concentration. Accordingly, when preparations containing carbamate agricultural chemicals are subjected to paddy water application, active ingredients can be spread and aggregated around water surface at a high concentration, and hence can be well adhered to the stem and leaf. It was also found that when an organic compound having the partition coefficient of the agricultural chemical to water of not less than 10^2 was added to the above preparation, it enabled to more effectively aggregate active ingredients around water surface and maintain them at a high concentration and for a longer period of time.

According to the present invention, it provides a water-floatable, aggregative solid agricultural preparation which comprises carrying (1) a carbamate agricultural chemical as the active ingredient (I) and (2) an organic compound (II) having a partition coefficient of said carbamate agricultural chemical (I) to water of not less than 10^2, on (3) a solid carrier, and optionally containing a thiolcarbamate insecticide such as cartap hydrochloride [1,3-bis(carbamoyl-thio)-2-(N,N-dimethylamino)-propane hydrochloride] or bensultap [S,S'-[2-(dimethylamino)-trimethylene]bis(benzenethiosulfonate)].

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PREFERRED EMBODIMENTS OF THE INVENTION

The carbamate agricultural chemicals (I) to be employed in this invention, may be any carbamate type insecticide or fungicide having spreadability and aggregative ability on water surface. Preferable examples of the carbamate agricultural chemicals (I) are compounds represented by the following formula:

$$R\text{-}NHCOO\text{-}Ar \qquad (I')$$

wherein R is a lower alkyl group and Ar is a phenyl or naphthyl group optionally having a substituent.

Examples of the lower alkyl group represented by R in the formula (I') are alkyl groups having 1 to 6 carbons such as methyl, ethyl, propyl, isopropyl, butyl, pentyl and hexyl. Substituents on the phenyl or naphthyl group represented by Ar may be such lower alkyl group as exemplified before in R, a halogen such as chlorine or bromine and an alkoxy group having 1 to 6 carbons.

Specifically, the carbamate agricultural chemicals (I) may be BPMC (O-sec-butylphenyl methylcarbamate), MIPC (2-isopropylphenyl-N-methylcarbamate), NAC (1-naphthyl-N-methylcarbamate), XMC (3,5-xylyl-N-methylcarbamate) and MTMC (m-tolyl-N-methylcarbamate), to which they are not limited. The carbamate

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agricultural chemicals (II) are added usually in about 30 - 0.5 parts by weight, preferably about 10 - 2 parts by weight, relative to 100 parts by weight of the total preparation.

The preparation of the present invention may optionally contain other agricultural chemicals than the above mentioned carbamate agricultural chemicals (I). Their preferable examples are insecticides or fungicides to be used for plant food application. Specifically, thiol-carbamate insecticides such as cartap hydrochloride or bensultap are conveniently added.

When cartap hydrochloride or bensultap having an excellent effect on a rice borer is added, the preparation can be utilized as a controlling agent against a brown leafhopper.

Examples of other usable agricultural chemicals to be incorporated in the preparation are insecticides such as MEP [O,O-dimethyl O-(4-nitro-m-tolyl)thiophosphate], diazinon [O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidyl)-thiophosphate], isoxathion [O,O-diethyl O-(5-phenyl-3-isoxazol)thiophosphate], malathon [S-(1,2-diearbethoxy-ethyl) O,O-dimethyl dithiophosphate] and a pyrethroid insecticide, or fungicides such as validamycins. These agricultural chemicals may be added singly or in mixture thereof, and usually added in about 0.1 - 15 parts by

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weight, preferably 0.2 - 5 parts by weight, to 100 parts by weight of the preparation.

The organic compound (II), another indispensable element of the present invention means, those having a partition coefficient of the carbamate active ingredient (I) to water of no less than 10^2. The compound (II) having no agricultural activity, but having a high boiling point is usually used. The compound (II) which is liquid at ordinary temperature (unless explicitly mentioned, the ordinary temperatures means 15°C hereunder) is preferred. In the present invention, the partition coefficient is the partition coefficient ordinarily used as a measure of lipophilic property. It means the constant in the partition law mentioned on page 209 of Encyclopedia Chimica Vol. 8, (edited by Encyclopedia Chimica Editor's Committee, Kyoritsu Shuppan, Japan, 1962). Namely, the partition law is defined in the Encyclopedia Chimica as "When a third material (solute) is dissolved in two liquids which are substantially immiscible each other and when they are coexisting, the concentration ratio in these two liquids becomes constant at a fixed temperature regardless of the concentration". The constant value in the partition law is called partition coefficient. The "partition coefficient" in the present invention means also the partition coefficient so defined. In the present

invention, the two liquids correspond to the water in paddy fields and the organic compound (II), and the solute corresponds to the active ingredient (I). By taking the concentration of the active ingredient (I) in the organic compound (II) at ordinary temperature as "Co" and the concentration of the active ingredient (I) in water as "Cw", the partition coefficient can be represented by Co/Cw. Namely the organic compound (II) in the present invention means those sufficing the equation of $Co/Cw \geq 10^2$. Although there is no upper limit of the partition coefficient Co/Cw of the organic compound (II) in the present invention, it is preferred to be no more than 10^7.

Summarizingly, the preferred condition of the organic compound (II) is $10^2 \leq Co/Cw \leq 10^7$ (at ordinary temperature. More preferred condition is $10^3 \leq Co/Cw \leq 10^6$ (at ordinary temperature). The ordinary temperature means 15°C in this case, too.

Among the organic compounds (II) having a partition coefficient to the active ingredient (I) of no less than 10^2, preferably no more than 10^7, the compounds in liquid at ordinary temperature and sufficing the following conditions are preferred ones:

(i) the solubility to water at ordinary temperature is no more than 5% (by weight).

(ii) boiling point is no lower than 160°C.

(iii) it dissolves no less than 1% (by weight of the

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active ingredient (I) at ordinary temperature.

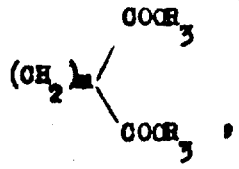
As the organic compounds (II) sufficing the above mentioned conditions, the followings are exemplified:

(i) fatty acid esters having the following formula (III):

$$R_1COOR_2$$

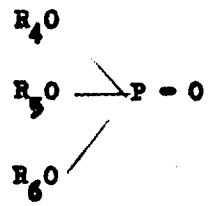
wherein R_1 represents a straight or branched alkyl group of C_{8-24} or an alkenyl group of C_{8-24} and R_2 represents a straight or branched alkyl group of C_{2-12}.

(ii) diesters having the following formula (IV):



wherein R_3 represents a straight or branched alkyl group of C_{2-12} and m represents an integer of 2-4,

(iii) phosphates having the following formula (V):



wherein R_4, R_5, and R_6 are same or different and re-

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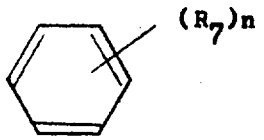
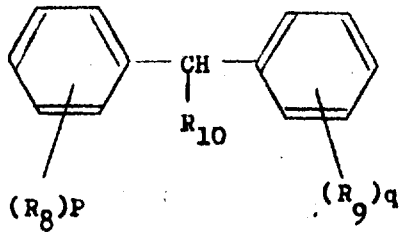
present a straight or branched alkyl group of C_{3-12}, a chlorinated alkyl group of C_{1-4} or a phenyl group,

(iv) alkylbenzenes having the following formula (VI):



wherein R_7 represents a straight or branched alkyl group of C_{2-16}, n means 1-4 showing the number of substituent R_7 groups,

(v) diphenylmethanes having the following formula (VII):



wherein R_8, R_9, and R_{10} represent a hydrogen atom or a straight or branched alkyl group of C_{1-5}, p and q means 1-3 showing the number of substituents R_8 and R_9 groups,

(vi) benzoates having the following formula (VIII):

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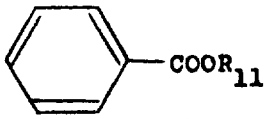
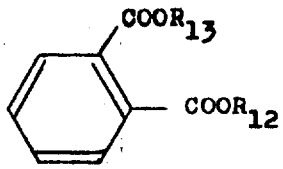


wherein R_{11} represents a straight or branched alkyl group of C_{1-12},

(vii) phthalate having to following formula (IX):



wherein each of R_{12} and R_{13} represents a straight and branched alkyl group of C_{1-12}.

Preferable examples of the alkyl group of C_{8-24} in R_1 of the fatty acid ester (III) are C_{9-19} alkyl groups such as nonyl, undecyl, tridecyl, pentadecyl, heptadecyl, Preferable examples of the alkenyl groups of C_{8-24} in R_1 are C_{15-19} alkenyl groups such as oleyl $\left[C_8H_{17}CH{=}CH(CH_2)_7-\right]$ or linoleyl $\left[C_5H_{11}CH{=}CH(CH_2)_7-\right]$. Preferably, the C_{2-12} alkyl groups of R_2 may be C_{3-8} alkyl groups such as butyl, amyl, hexyl or heptyl. Specific example of the fatty acid esters (III) are amyl laurate, amyl myristate, butyl palmitate, amyl palmitate, hexyl palmitate, butyl stearate, amyl stearate, hexyl stearate, butyl oleate, amyl oleate

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and butyl linolate.

Preferably examples of the C_{2-12} alkyl groups in R_3 of the diesters (IV) are C_{2-10} alkyl groups such as ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl. Specifically, the diesters (IV) may be diethyl succinate, dipropyl succinate, dibutyl, succinate, diamyl succinate, dioctyl succinate, diethyl glutamate, dibutyl glutamate, diamyl glutamate, dioctyl glutamate, dibutyl adipate, diamyl adipate or dioctyl adipate.

Preferable examples of the C_{3-12} alkyl groups in (R_4, R_5, and R_6) of the phosphate (V) are C_{4-9} alkyl groups such as butyl, amyl, hexyl or octyl. In the same structure, the C_{1-4} chlorinated alkyl groups (R_4, R_5, R_6) are preferably C_{2-3} chlorinated alkyl groups such as trichloroethyl or trichloropropyl. Accordingly, the phosphate esters (V) may be tributyl phosphate, triamyl phosphate, trioctyl phosphate, butyl diphenyl phosphate, octyl diphenyl phosphate or tri(chloroethyl) phosphate.

Preferable examples of the C_{2-16} alkyl groups (R_7) of the alkylbenzene (VI) are C_{2-10} alkyl groups such as ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, tert-amyl, octyl or decyl. The compounds (VI) are those having 1-4 same or different substituents mentioned above on the benzene ring. Specific examples of the alkylbenzenes (VI) are diethyl-

benzene, diisopropylbenzene, triisopropylbenzene, tert-butylbenzene, di(tert-butyl)benzene, diamylbenzene, triamylbenzene, tetraamylbenzene, tert-amylbenzene, di(tert-amyl)benzene, octylbenzene, dodecylbenzene and didodecylbenzene.

Examples of the C_{1-3} alkyl groups (R_8, R_9, R_{10}) of the diphenylmethanes (VIII) are methyl, ethyl, propyl or isopropyl. When the diphenylmethane (VII) has two or three of R_8 having a C_{1-3} alkyl group, these C_{1-3} alkyl groups may be the same or different. Similarly, in case where the diphenylmethane (VII) has two or three of R_9 having a C_{1-3} alkyl, they may be the same or different. Accordingly, the diphenylmethane (VII) is exemplified by phenylxylylethane, phenylxylylpropane, trixylylethane, dixylylmethane and diisoxylylethane.

The C_{1-12} alkyl groups (R_{11}) of the benzoate (VIII) are preferably C_{1-8} alkyl groups such as methyl, ethyl, butyl, amyl, hexyl or octyl. Specifically, the benzoate (VIII) may be methyl benzoate, ethyl benzoate, butyl benzoate, amyl benzoate, hexyl benzoate, octyl benzoate or nonyl benzoate.

The C_{1-12} alkyl groups (R_{12}, R_{13}) of the phthalate (IX) are preferably C_{1-8} alkyl groups such as methyl, ethyl, butyl, amyl, hexyl or octyl. Specifically, the phthalate (IX) may be dimethyl phthalate, diethyl phthalate, dibutyl phthalate or dioctyl phthal-

ate.

The organic compounds (II) may be used singly or in mixture thereof.

The organic compounds (II) are usually used in about 5 - 0.1 parts by weight, preferably about 3 - 0.2 parts by weight, to one part by weight of the carbamate type active ingredient (I).

Any solid carriers which are able to give a water-floatability to the preparation can be used as the carriers of this invention. The solid carriers having a particle diameter of 60 - 1000 μm are generally preferable. The use of the solid carrier having a particle diameter of less than 60 μm is not desirable generally because of safety and hygienic issues and difficulty in due to a whirling of powders. The use of the solid carrier having a particle diameter of more than 1000 μm is also not desireble because of the low drying efficiency due to floatability and spreadability of the preparation on a water surface although a whirling of powders can be suppressed completely. More preferable particle diameter of the carrier is in the range of 100 - 800 um. Examples of the solid carriers are those having water-floatability in themselves, such as perlite, vermiculite, pumice (e.g. Klite No. 3(R) (KANSAI JARI KK)), walnut powder ob-

tainable by pulverizing the shell of a walnut, or wooden powder, and also those which sink per se but become water-floatable by a combination use with a water repellent, such as crushed or otherwise comminuted sand product (hereinafter sometimes referred to briefly as crushed sand) [e.g. those disclosed in Japanese Unexamined Publication No. (1986) - 286302], silica sand [e.g. river sand (Hayashi Kasei, Japan)], rhyolite [e.g. Hinoyalite (Hinoya Shokai, Japan), Kagalite (Tango Kensetsu, Japan)], granular diatomite [e.g. Ceratom(R) (Kakiuchi Shoji, Japan)], and other water soluble granular mineral carriers with particle diameter of 60 - 1000 um such as granular ammonium sulfate or granular urea. Among these carriers, perlite means a product prepared from obsidian, perlite or other vitreous volcanic rocks which swell by heating, and is commercially available with various grades. Examples of commercial products of perlites are Topuko® #34, Topuko(R) #54, Topuko(R) #71 [available from Toko Perlite Kogyo Co., Ltd. Japan] and Perlite Meigara type 1 [available from Ube Industries, Ltd, Japan]. Vermiculite has the structure like $Mg(Si, Al)O(OH)Mg. H_2O$ and is available with various grades with or without calcination. Walnut flour [Nippon Walnut Co., Ltd. Japan] is exemplified as a commercial product of the

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walnut powder. Even in case of the aforesaid solid carriers having specific gravity of more than 1, they become water-floatable by the combination with a water repellent, magnesium stearate or the like. As such solid are conveniently used crushed sand, preferably crushed sand with a particle diameter of 60 - 1000 μm (which is available by crushing more finely according to the method disclosed in the Japanese Unexamined Patent Publication No. 61(1986)-286302, and pumice. Particularly preferred are crushed sand of particle diameter of 60 - 1000 μm. The solid carriers having a preferable particle diameter of 60 - 1000 um are easily available from the market. It is also possible to obtain the carriers having a desired particle diameter by sizing or screening using conventional vibratory filtration or cyclone method. Besides, basalt, andesite, sandstone, quartz porphyry and those having a stone quality similar thereto are used as the crushed sand mentioned above. Such raw ore can be pulverized after removing top soil and other impurities by using, for example, scarping screen, ripple flow screen and the like. A similar process to the manufacture of grinded bone materials is utilized in reducing a raw ore into powder. A grinded powder of a raw ore is obtained,

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for example, at first by getting rid of surface soil and other impurities, and then grinding them gradually by using known grinders in order, for example, jaw crusher (crusher for crushing a big lump), cohen crusher for crushing a medium size lump) and impera breaker (crusher for getting fine pieces), and thereafter classifying them by air separator.

Those solid carriers which are able to give a floatability to the preparation are usually used in about 30 - 98 weight parts, preferably 65 - 95 weight parts, to 100 weight parts of the total preparation. However, it is also possible, if desired, to use, in addition to the solid carriers mentioned above which are appropriate to give a floatability to the preparations, one or more kinds of other solid carriers such as vegetable powders, clays, talcs, silicas (diatomite, etc.), zeolite, river sand, calcium carbonate and the like, in an extent of not disturbing the effect of this invention. In this invention, it is desirable to mix thoroughly the carbamate agricultural chemical and, if desired, the other active component, with the aforesaid solid carriers and more preferably to make the active components adhere to or adsorb in the solid carriers or to coat the solid carriers with the active components. In order to im-

prove adherence of those components, it is possible to add a conventional binding agent, such as sodium carboxymethylcellulose (CMC-Na), polyvinyl alcohol, starch, polyoxyethylene waxes (e.g. polyoxyethylene-nonylphenylether, polyoxyethylene glycol, etc.) and the like. When a water repellent of this invention, such as hydrophobic aerosil (e.g. Aerosil(R) R-972 (Nippon Aerosil KK), magnesium stearate, purified talc, silicon oil and the like is added to the preparation, it is effective to prolong the floatability of the preparation and also to give floatability to the solid carrier with a specific gravity of more than 1. TThe amount of the water repellent is usually about 0.05 - 5 weight parts, preferably 0.1 - 2 weight parts, to 100 weight parts of the preparation.

It is also possible to add a higher fatty acid in order to improve water repellent properties and// or water-floatability of the preparations. Preferable exemples of the higher fatty acids are those having 8 to 20 carbons, especially such as stearic acid, palmitic acid and lauric acid. These fatty acids can be used singly or in mixture thereof. If need be, it is also possible to add, a surfactant (e.g. polyoxyetyrenephenol), and an antioxidant (e.g. isopropyl acid phosphate), a flow auxiliary agent, a lubricant, a

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stabilizer (e.g. phosphonic acid, tartaric acid, etc.) etc. to an extent that the effect of this invention is not disturbed.

The preparation of this invention can be manufactured by mixing the carbamate agricultural chemical (I) and the organic compound (II) with the solid carrier in accordance with the conventional method. It is preferable, by mixing them thoroughly to make the active component adhere to or adsorb in the solid carrier or to coat the solid carrier with the active component. In the mixing process the carbamate agricultural chemical (I) and optionally the other active components are usually added to the solid carrier in a conventional mixer, such as drum type mixer, and then mixed by further adding the aforementioned organic compound (II) having a partition coefficient of not less than 10^2. Alternatively, it is also possible to mix first the carrier and the binding agent and then to add the main active ingredient thereto in order to adhere it to the carrier or to coat the carrier with it. In such way, the order of the mixing is not limited.

The preparations are desirable to be manufactured as granular preparations in accordance with the conventional method. However, it is also possible to

prepare them as fine granules, subtilized granules or powdery granules, which have more fine particles.

In preparing the granular preparations, the conventional method can be used, for example, such as the wet granulation method which follows the processes of addition of water, kneading, granulating and drying, after mixing in the mixer such as the aforesaid drum-type mixer.

The dosage of the agricultural preparation of this invention varies, depending upon place, timing and method of application, targeted blights, crops, etc. However, it is generally about 0.05 - 50 g, preferably 2 - 20 g, more preferably 8 - 16 g per one are of a paddy field as the active components contained therein, inclusive of the carbamate agricultural chemical and the optional other active component.

This invention is further illustrated by examples and test examples.

In the following examples, "part" means "part by weight".

Example 1

A homogeneous mixture of 3.0 parts of BPMC and 2.0 parts of octyldiphenylphosphate (hereinafter

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abbreviated a ODP) was poured into 94.8 parts of pumice having a particle diameter of 300 - 600 um in a drum mixer under rotating, to carry the mixture on pumice, 0.2 part of magnesium stearate (abbreviated as St-Mg) to the resultant were added to obtain the coated granular preparation.

Example 2

A homogenous mixture of 4.0 parts of MIPC and 4.0 parts of dioctyl adipate (abbreviated as DOA) was poured into 93.0 parts of Kagalite having a particle diameter of 100 - 500 um in a drum mixture under rotating, to carry the mixture on Kagalite, followed by addition of 1.0 part of purified talc. Thus the coated granular preparation was obtained.

Example 3

A homogenous mixture of 4.0 parts of BPMC and 4.0 parts of ODP was poured into 86.6 parts of CERATOM® having a particle diameter of 300 - 700 μm in a drum mixer under rotating, to carry the mixture on CERATOM, followed by addition of 4.0 parts of cartap hydrochloride (abbreviated as CT) and 1.2 parts of PEG-400. Then, 0.2 part of AEROSIL® R-972 were mixed with the resultant to obtain the coated granular preparation.

Ref. 2657

Example 4

A homogenous mixture of 4.0 parts of MIPC and 4.0 parts of ODP was poured into 86.2 parts of CERATOM® in a drum mixer under rorating followed by addition of 4.0 part of BENSULTAP and 1.2 parts of PEG-200. Then, 0.3 part of St-Mg were mixed with the resultant to obtain the coated granular preparation.

Example 5

A homogeneous mixture of 2.5 parts of NAC and 1.5 parts of diethyl phthalate was poured with 92.5 parts of granular ammonium sulfate in a drum mixer under rotating, followed by addition of 2 parts of bensultap. Then 1.5 parts of purified talc were mixed with the resultant to obtain the coated granular preparation.

Example 6

A homogenous mixture of 4.0 parts of BPMC and 4.0 parts of ODP was poured into 86.8 parts of CERATOM® having a particle diameter of 150 - 550 µm in a drum mixer under rotating, followed by addition of 4.0 parts of CT and 1.0 part of validamycin A. Then, 0.2 part of AEROSIL® R-972 were mixed with the resultant to obtain the granular preparation.

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Example 7

A homogenous mixture of 4.0 parts of MIPC and 4.0 parts of DOA was poured into 86.0 parts of Hinoyalite in a drum mixer under rotating, followed by addition of 4.0 parts of bensultap and 1.5 parts of validamycin A. Then, 0.5 part of St-Mg were well mixed with the resultant to obtain the granular preparation.

Example 8

A homogenous mixture of 2.0 parts of BPMC and 1.0 parts of diethyl phthalate was poured into 95.8 parts of granular urea in Nauta mixer under rotating, followed by addition of 0.5 parts of validamycin A. Further, 0.3 part of silicon oil and 0.4 part of white carbon were added to obtain the granular preparation.

Example 9

A homogenous mixture of 3.0 parts of BPMC, 5.0 parts of ethyl benzoate and 3.0 parts of MEP was added to 88.7 parts of CERATOM® having a particle diameter of 250 - 600 μm in Nauta mixer under rotating, followed by well mixing with 0.3 part of AEROSIL® R-972 to obtain the coated granular preparation.

Example 10

In a rotating drum mixer, 4.0 parts of BPMC and 4.0 parts of ODP were added to 86.3 parts of CERATOM® having a particle diameter of 300 - 700 μm, followed by addition of 1.5 parts of polyethylenenonylphenylether. Then, 0.2 part of AEROSIL® R-972 were mixed with the resultant to obtain the granular preparation.

Example 11

To 89.25 parts of pumice having a particle diameter of 300 - 500 μm in a drummmixer was poured a homogenous mixture of 4.0 parts of melted BPMC, 2.0 parts of DOA and 0.25 part of isopropyl acid phosphate. After mixing, 4.0 parts of CT were added to the resultant mixture, followed by addition of 0.5 part of AEROSIL® R-972 to obtain the coated granular preparation.

The following is the examples of the control preparations which do not belong to this invention.

Control Preparation 1 (corresponding to Example 3)

4.0 Parts of ODP, 4.0 parts of CT, 0.2 part of AEROSIL® R-972 and 1.2 parts of PEG-400 were added to 77.6 parts of clay, which were thoroughly mixed in a drum mixer. To the resultant mixture were further added 12 parts of water, kneaded, granulated and

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dried to obtain the preparation having a particle diameter of 800 μm.

Control Preparation 2 (corresponding to Example 4)

4.0 Parts of ODP, 4.0 parts of bensultap, 1.5 parts of PEG-200 and 0.3 parts of St-Mg were added to 79.2 parts of clay, which were thoroughly in a drum mixer. Further, 12 parts of water were added to the mixture, kneaded, granulated and dried to obtain the preparation having a particle diameter of 500 μm.

Control Preparation 3 (corresponding to Example 9)

3 Parts of MEP, 5 parts of benzyl alcohol and 0.3 part of AEROSIL® R-972 were added to 79.2 parts of clay, which were thoroughly mixed in Nauta mixer. To the resultant mixture were added 12.5 parts of water, kneaded, granulated and dried to obtain the granular preparation having a particle diameter of 700 μm.

Efficacy test against Nilaparvata lugens

24 - 30 imagos of female Nilaparvata lugens were released for 5 - 6 days on 22 days (repeat 1) - 29 days (repeat 2) before application of the drug preparation in a large greenhouse made by acryl resin to give an oviposition onto rice plant (species: Nippon bare, stage of growth at the time when the

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drug was applied: optimum fillering stage, cultivation density: 20 stumps/m^2) transplanted to the bed (1 m x 1 m) in said green house. A specified amount of each of the aforesaid preparations was sprayed equally by hand onto the rice plant with the target to the insects mainly consisting of larvae of the next generation stemming from said oviposition.

The number of surviving insects on the 4 stumps at the center of the bed was counted on the day before application of the preparation and each of the one and three days after application of the preparation, and the efficacy of the drugs was evaluated in terms of an average by determining the corrected reproduction index in accordance with the following formula: C.R.I. (Corrected Reproduction Index): 100 x (Xi/Xo)/(Ci/Co) wherein Xi and Xo mean the numbers of surviving insects at each drug application area on one day after the application, respectively, and Ci and Co mean the numbers of surviving insects at non-drug application area on one day after the drug application and on the day before the drug application, respectively. The corrected reproduction index 100 indicates that no efficacy of the preparation was observed.

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TABLE

Results of Efficacy Test against Nilaparvata lugens

Preparations	Amount applied (ai g/10 are)	C R I	
		1 day after application	3 days after application
Example 3	160	1.9	0.9
"	240	0.8	0.4
Example 4	160	0.7	0.7
Example 4	240	0.2	0.1
Example 6	160	0.9	1.3
"	240	1.2	0.5
Example 7	160	2.1	1.1
"	240	0.8	0.6
Control Preparation 1	160	33.4	35.7
"	240	29.7	25.8
Control Preparation 2	160	19.9	24.0
"	240	21.4	22.5
Control Preparation 4	160	18.5	19.0
"	240	20.7	16.4

Note: The efficacy of the drug is indicated by the corrected reproduction index (CRI) (average of 2 repeats).

ai: indicates the amount of the pure active substance.

Ref. 26530

Efficacy test against Pellicularia sasakii

40 mg of the preparation was sown equally by hand on the rice plant (species: Shinsenbon, stage of growth at the time when the preparation was applied: 8 - 9 weeks) transplanted into pot (1/10,000 a), on which Pellicularia sasakii was inoculated. Those treated with the preparation one day after inoculation is referred to as the cure test and those treated with the preparation 1 hour after inoculation is referred to as the prophylactic test.

The efficacy was determined by measuring the distance from the soil surface of the rice plant up to top of the disease punctum at 10 days after infection.

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Table

Results of Efficacy Test against Pellicularia sasakii

The preparations	Prophylactic Effect (cm)	Cure Effect (cm)
The granular preparation of Example 6	0.00	1.52
The granular preparation of Example 7	0.00	1.18
The granular preparation of Example 8	0.01	1.04
The control preparation 1	15.98	19.66
The control preparation 4	10.67	16.07
Control	17.53	20.5

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WHAT WE CLAIM IS:

1. A water-floatable, aggregative solid agricultural composition which comprises carrying

(1) a carbamate agricultural chemical having the formula of R-NHCOO-Ar wherein R is a lower alkyl group and Ar is a phenyl or naphthyl group which may be substituted by the group consisting of an alkyl group having 1 to 6 carbon atoms, a halogen and an alkoxy group having 1 to 6 carbon atoms and having spreadability and aggregative ability on water surface as the active ingredient, in an amount of 0.5-30 parts by weight relative to 100 parts by weight of the total composition and

(2) an organic compound having a partition coefficient of said carbamate agricultural chemical (1) to water of not less than 10^2, a solubility to water at ordinary temperature which is no more than 5% (by weight), a property which can dissolve not less than 1% (by weight) of said carbamate agricultural chemical, no agricultural activity and a high boiling point which is not lower than 160°C and being liquid at ordinary temperature, in an amount of 0.1 - 5 parts by weight to one part by weight of said carbamate agricultural chemical, on (3) a solid carrier.

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4. A composition of Claim 1 which further contains validamycin A.

5. A composition of Claim 1 in which the solid carrier has a particle diameter of 60 - 1000 µm.

6. A composition of Claim 1 in which the solid carrier is a crushed sand having a particle diameter of 60 - 1000 µm.

7. A composition of Claim 1 which further contains a water repellent.

8. A composition of Claim 2 which further contains validamycin A.

9. A composition of Claim 2 which further contains a water repellent.

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