PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to Fumigation and Fumigating Charges

We, JOHN STOCKS FLANDERS, of "Hillcrest", Bowfield Road, West Kilbride, Ayrshire, and ELWYN JONES, of 41, South Beach Road, Ardrossan, Ayrshire, both British subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

The present invention relates to the art of fumigating with pesticidal compounds, and more particularly to the provision of an improved charge for the thermal production of fumes of pesticidal compounds that are capable of vaporisation when suitably heated. The invention is especially valuable for the purpose of fumigating with combustible pesticidal compounds or pesticidal compounds easily decomposed when overheated. The invention, for instance, facilitates the economical production of a fume comprising an aerosol of the condensed vapour of a pesticidal compound which can deposit on the boundary surfaces of a closed space in which the fume is generated so as to produce a thin layer of the pesticidal compound that will be active long after the atmosphere is clear of the actual fumes.

One example of a pesticide capable of depositing such a layer when a suitable fumigation method is applied to volatilise it, is the powerful insecticide alpha-alpha-bis(chloropheny1)-beta-beta-beta-trichloroethane, generally known as D.D.T. A further example is the powerful insecticide gamma-benzene hexachloride which can be applied in the form of a smoke by volatilisation from hot plates or by other heating methods.

A combustible candle fumigator, similar to the familiar sulphur candle, would be a very convenient means for producing the fumes of a vaporisable pesticidal compound, but in the case of many pesticides it would not be possible to make up a candle in which a pesticide is drawn into a flame for the purpose of volatilising it, since the pesticide would thereby be decomposed or burned with the formation of useless decomposition or combustion products, whereas in the case of the sulphur candle the active material is the sulphur dioxide produced by the burning of the sulphur.

It is known that the thermal decomposition of ammonium nitrate can be sensitised by admixture of the ammonium nitrate with various salts of chromic acid, with the result that when a merely local element of a mass of the composition at ordinary temperature is strongly heated by means of a red hot object or the like, a self-sustained flameless gas producing exothermic decomposition progresses throughout the mass at ordinary pressure. Potassium bichromate, chromate and ammonium bichromate are examples of salts of chromic acid having this action.

The temperatures attained in the mass as the result of the decomposition are, generally speaking, much below those experienced in ordinary instances of combustion. The present invention is based on the discovery that while the heat vaporisable pesticidal compounds are typically oxidisable substances and the salt of chromic acid contains available oxygen, the pesticidal compound can be vaporised without any substantial destruction when it is present in admixture in a composition comprising ammonium nitrate and a salt of chromic acid adapted to render the ammonium nitrate in the mixture capable of such self-sustained exothermic decomposition.

According to the present invention therefore an improved fumigating charge consists of a mixture comprising a thermally vaporisable pesticidal compound, ammonium nitrate and an ammonium nitrate-sensitising salt of chromic acid in amount sufficient to render the composition capable of propagating throughout itself at ordinary pressure the exothermic decomposition of the ammonium nitrate therein, when the mixture is merely locally raised to a high temperature by the application of an incandescent object or

[Price 1/-]

the like.

A cartridge made up from the composition and provided with a waterproof casing may advantageously be employed, and such cartridge may advantageously include a small piece of fuse or of match composition or other igniting composition in contact with the fumigating charge in order to facilitate the ignition of the latter from an ordinary domestic friction match. The fumigating charge is preferably in compact form, and for its production the pulverulent mixture of ingredients may be subjected to compression. Otherwise the mixture may be made into compact form with the aid of a binder or bonding agent, for instance, a nitrocellulose composition, and may be extruded or moulded into form. The cartridge comprising the fumigating charge may conveniently be wrapped up in paper, and the wrapped cartridge then dipped in wax or other waterproofing medium.

When a local portion of the charge is strongly heated by the ignition of the match compositon or the like or the piece of fuse, or by touching it with a piece of red hot metal or the like, a gas evolving decompositon accompanied by the evolution of the pesticidal fume and little carbon fume if any, and quite unaccompanied by flame, will propagate itself through the charge. The fumigating charges provided according to the present invention are therefore both safe and convenient for application in confined spaces even when easily inflammable objects are present in the confined space.

The invention is illustrated by the following examples, in which the parts mentioned are parts by weight.

Example 1.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is compacted by pressure into the form of a rod of about 1 centimetre diameter and considerably greater length, a small piece of fuse being inserted in the mixture so as to extend from one end of the rod inwardly for a considerable distance. The composite rod so obtained is wrapped in manilla paper and dipped in a molten paraffin wax melting at about 50° C. maintained at a temperature not exceeding about 75° C. The end provided with the fuse is marked so that the wrapper can be broken to expose the end of the cartridge containing the fuse when it is desired to use the cartridge.

Example 2.

The procedure is the same as in Example 1 except that in place of 10 parts gamma-benzene hexachloride there are employed 10 parts alpha-alpha-bis (para-chlorophenyl)-beta-beta - beta - trichloroethane (D.D.T.)

Example 3.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is mixed with a nitrocellulose solution made from 50 parts quarter second industrial nitrocellulose, 48 parts dibutyl phthalate and 2 parts diphenylamine, the ratio of the amounts of the powder mixture and of the nitrocellulose solution being 7:35 by weight. The resulting paste is extruded at suitably raised temperature not exceeding 100° C. to the desired diameter and cut into suitable lengths before it cools. A small bead of a match head composition in the form of a paste containing a solution of a binding agent is applied at one end of each of the cut rods, and after this has dried off the rod is wrapped in paper.

Dated the 4th day of June, 1945.
J. W. RIDSDALE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to Fumigation and Fumigating Charges

We, John Stocks Flanders, of "Hillcrest", Bowfield Road, West Kilbride, Ayrshire, and Elwyn Jones, of 41, South Beach Road, Ardrossan, Ayrshire, both British subjects, and Imperial Chemical Industries Limited, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the art of fumigating with pesticidal compounds, and more particularly to the provision of an improved composition for the thermal production of fumes of pesticidal compounds that are capable of vaporisation when suitably heated. The invention is especially valuable for the purpose of

fumigating with combustible pesticidal compounds or pesticidal compounds easily decomposed when overheated. The invention, for instance, facilitates the economical production of a fume comprising an aerosol of the condensed vapour of a pesticidal compound which can deposit on the boundary surfaces of a closed space in which the fume is generated so as to produce a thin layer of the pesticidal compound that will be active long after the atmosphere is clear of the actual fumes.

One example of a pesticide capable of depositing such a layer when a suitable fumigation method is applied to volatilise it, is the powerful insecticide alpha-alpha-bis-(para-chlorophenyl)-beta-beta-beta-trichloroethane, generally known as D.D.T. A further example is the powerful insecticide gamma-benzene hexachloride which can be applied in the form of a smoke by volatilisation from hot plates or by other heating methods.

A combustible candle fumigator, similar to the familiar sulphur candle, would be a very convenient means for producing the fumes of a vaporisable pesticidal compound, but in the case of many pesticides it would not be possible to make up a candle in which a pesticide is drawn into a flame for the purpose of volatilising it, since the pesticide would thereby be decomposed or burned with the formation of useless decomposition or combustion products, whereas in the case of the sulphur candle the active material is the sulphur dioxide produced by the burning of the sulphur.

It is known that the thermal decomposition of ammonium nitrate can be sensitised by admixture of the ammonium nitrate with various salts of chromic acid, with the result that when a merely local element of a mass of the mixture of these components at ordinary temperature is strongly heated by means of a red hot object or the like local heating means, a self-sustained flameless gas producing exothermic reaction progresses throughout the mass at ordinary pressure. Salts of chromic acid having this action are referred to briefly hereinafter as "ammonium nitrate decomposition sensitising salts of chromic acid." Potassium bichromate, potassium chromate and ammonium bichromate are examples of salts of chromic acid having this action.

The temperature attained in the mass as the result of the reaction are, generally speaking, much below those experienced in ordinary instances of combustion. The present invention is based on the discovery that while the heat vaporisable pesticidal compounds are typically oxidisable substances, and while ammonium nitrate contains, and the salt of chromic acid may contain, available oxygen (ammonium bichromate may be held not to contain available oxygen if its decomposition proceeds in a straight-forward manner), the pesticidal compound can be vaporised without any substantial destruction when it is present in admixture in a composition undergoing thermal decomposition and comprising ammonium nitrate and a salt of chromic acid adapted to render the ammonium nitrate in the mixture capable of such self-sustained exothermic reaction.

According to the present invention therefore the improved fumigating composition consists of a mixture comprising a thermally vaporisable pesticidal compound, ammonium nitrate and an ammonium nitrate decomposition sensitising salt of chromic acid as hereinbefore defined in amount sufficient to render the composition capable of propagating throughout itself at ordinary atmospheric pressure an exothermic reaction when initiated by local heating.

The said mixture may also include china clay.

A cartridge made up from the composition and provided with a waterproof casing may advantageously be employed, and such cartridge may advantageously include a small piece of fuse or of match composition or other igniting composition in contact with the fumigating charge in order to facilitate the ignition of the latter from an ordinary domestic friction match. The fumigating charge is preferably in compact form, and for its production the pulverulent mixture of ingredients may be subjected to compression. Otherwise the mixture may be made into compact form with the aid of a binder or bonding agent, for instance, a nitrocellulose composition, and may be extruded or moulded into form. The cartridge comprising the fumigating charge may conveniently be wrapped up in paper, and the wrapped cartridge dipped in wax or other waterproofing medium.

When a local portion of the charge is strongly heated by the ignition of the match composition or the like or the piece of fuse, or by touching it with a piece of red hot metal or the like local heating means, a gas evolving decomposition accompanied by the evolution of the pesticidal fume, and little carbon fume, if any, and quite unaccompanied by flame, will propagate itself through the charge. The fumigating charges provided according to the present invention are therefore both safe and convenient for application in confined space even when easily inflam-

mable objects are present in the confined space.

The invention is illustrated by the following examples, in which the parts mentioned are parts by weight, except where otherwise indicated.

EXAMPLE 1.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is compacted by pressure into the form of a rod of about 1 centimetre diameter and considerably greater length, a small piece of fuse being inserted in the mixture so as to extend from one end of the rod inwardly for a considerable distance. The composite rod so obtained is wrapped in manilla paper and dipped in a molten paraffin wax melting at about 50° C. maintained at a temperature not exceeding about 75° C. The end provided with the fuse is marked so that the wrapper can be broken to expose the end of the cartridge containing the fuse when it is desired to use the cartridge.

EXAMPLE 2.

The procedure is the same as in Example 1 except that in place of 10 parts gamma-benzene hexachloride there are employed 10 parts alpha-alpha-bis-(para-chlorophenyl)-beta-beta-beta-trichloroethane (D.D.T.)

EXAMPLE 3.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is mixed with a nitrocellulose solution made from 50 parts quarter second industrial nitrocellulose, 48 parts dibutyl phthalate and 2 parts diphenylamine, the ratio of the amounts of the powder mixture and of the nitrocellulose solution being 65:35 by weight. The resulting paste is extruded at suitably raised temperature not exceeding 100° C. to the desired diameter and cut into suitable lengths before it cools. A small bead of a match head composition in the form of a paste containing a solution of a binding agent is applied at one end of each of the cut rods, and after this has been dried off the rod is wrapped in paper.

EXAMPLE 4.

A fumigating composition to be used in powder form is made up as follows:—
75 parts of a mixture consisting of 90 parts ammonium nitrate and 10 parts potassium chromate, are mixed with 25 parts of a crude gamma benzene hexachloride, and 93 parts of the resulting mixture is mixed with 7 parts of china clay.

EXAMPLE 5.

A fumigating composition to be used in powder form is made up as follows:—
75 parts of a mixture consisting of 90 parts ammonium nitrate and 10 parts potassium chromate, are mixed with 25 parts of pure gamma-benzene hexachloride, and 97 parts of the resulting mixture is mixed with 3 parts of china clay.

EXAMPLE 6.

A fungicidal composition to be used in powder form is made up as follows:—
80 parts of a mixture consisting of 90 parts ammonium nitrate and 10 parts potassium chromate, are mixed with 20 parts of the fungicide pentachlorophenol.

The description "quarter second industrial" of the nitrocellulose used in Example 3 has reference to the viscosity and nitrogen content of the nitrocellulose, and indicates the time that would be taken for a $\frac{5}{16}$" steel ball to fall 10" through a 12½% solution of a nitrocellulose of nitrogen content not exceeding 12.3% in a mixed solvent consisting of 25% methylated spirits, 20% ethyl acetate and 55% benzene at 25° C. The determination is actually carried out in 25% solution, for which the time of the descent of the ball is 2½ to 3½ seconds. In an alternative method of determination 40 grams of the nitrocellulose are made up into solution in 100 c.c. of acetone of 95% concentration by volume, this solution having a viscosity at 20° C. of approximately 10 c.g.s. units for a "quarter second" nitrocellulose.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A fumigating composition consisting of a mixture comprising a thermally vaporisable pesticidal compound, ammonium nitrate and an ammonium nitrate decomposition sensitising salt of chromic acid as hereinbefore defined in amount sufficient to render the composition capable of propagating throughout itself at ordinary atmospheric pressure an exothermic reaction when initiated by local heating.

2. A fumigating composition as claimed in claim 1 wherein the said mixture includes china clay.

3. A fumigating composition as claimed in claim 1 or 2 in the form of a compressed rod.

4. A fumigating composition as claimed in claim 3 wherein the compressed rod is provided with a waterproof casing.

5. A fumigating composition as claimed in claim 3 or 4 wherein the compressed rod

mable objects are present in the confined space.

The invention is illustrated by the following examples, in which the parts mentioned are parts by weight, except where otherwise indicated.

EXAMPLE 1.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is compacted by pressure into the form of a rod of about 1 centimetre diameter and considerably greater length, a small piece of fuse being inserted in the mixture so as to extend from one end of the rod inwardly for a considerable distance. The composite rod so obtained is wrapped in manilla paper and dipped in a molten paraffin wax melting at about 50° C. maintained at a temperature not exceeding about 75° C. The end provided with the fuse is marked so that the wrapper can be broken to expose the end of the cartridge containing the fuse when it is desired to use the cartridge.

EXAMPLE 2.

The procedure is the same as in Example 1 except that in place of 10 parts gamma-benzene hexachloride there are employed 10 parts alpha-alpha-bis-(para-chlorophenyl)-beta-beta - beta - trichloroethane (D.D.T.)

EXAMPLE 3.

A mixture of 90 parts pulverised ammonium nitrate, 10 parts gamma-benzene hexachloride and 10 parts potassium chromate in powder form is mixed with a nitrocellulose solution made from 50 parts quarter second industrial nitrocellulose, 48 parts dibutyl phthalate and 2 parts diphenylamine, the ratio of the amounts of the powder mixture and of the nitrocellulose solution being 65:35 by weight. The resulting paste is extruded at suitably raised temperature not exceeding 100° C. to the desired diameter and cut into suitable lengths before it cools. A small bead of a match head composition in the form of a paste containing a solution of a binding agent is applied at one end of each of the cut rods, and after this has been dried off the rod is wrapped in paper.

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The description " quarter second industrial " of the nitrocellulose used in Example 3 has reference to the viscosity and nitrogen content of the nitrocellulose, and indicates the time that would be taken for a $\frac{5}{16}$" steel ball to fall 10" through a 12½% solution of a nitrocellulose of nitrogen content not exceeding 12.3% in a mixed solvent consisting of 25% methylated spirits, 20% ethyl acetate and 55% benzene at 25° C. The determination is actually carried out in 25% solution, for which the time of the descent of the ball is 2½ to 3½ seconds. In an alternative method of determination 40 grams of the nitrocellulose are made up into solution in 100 c.c. of acetone of 95% concentration by volume, this solution having a viscosity at 20° C. of approximately 10 c.g.s. units for a " quarter second " nitrocellulose.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A fumigating composition consisting of a mixture comprising a thermally vaporisable pesticidal compound, ammonium nitrate and an ammonium nitrate decomposition sensitising salt of chromic acid as hereinbefore defined in amount sufficient to render the composition capable of propagating throughout itself at ordinary atmospheric pressure an exothermic reaction when initiated by local heating.

2. A fumigating composition as claimed in claim 1 wherein the said mixture includes china clay.

3. A fumigating composition as claimed in claim 1 or 2 in the form of a compressed rod.

4. A fumigating composition as claimed in claim 3 wherein the compressed rod is provided with a waterproof casing.

5. A fumigating composition as claimed in claim 3 or 4 wherein the compressed rod

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is provided with a small piece of igniting composition.

6. A fumigating composition substantially as described and with reference to the foregoing examples.

Dated the 6th day of March, 1946.

J. W. RIDSDALE,
Solicitor for the Applicants.

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