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PEST CONTROL AGENTS

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11 Claims. (Cl. 167—30)

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This invention relates to pest control agents and more particularly to those for the control of fungi, bacteria, marine organisms and other pests.

The agents heretofore used comprise substantially water-insoluble metallic salts of naphthenic acid and other similar organic substantially water-insoluble acids. Copper and zinc salts have been most widely used in this connection to prevent or minimize the deterioration of cellulosic material due to the ravages of micro-organisms, such as fungi and bacteria. They have also been employed to protect cellulosic articles, protein materials and living plants from the ravages of other inimical organisms, such as insects, bacteria, actinomycetes, etc.

Herein the term "pest control" is used in its broadest sense with respect to all known types of pests to which articles of commerce and economic crops are vulnerable and to the toxicant salts of other metals as well as copper and zinc to which reference has been made.

While toxicant metallic salts have been widely used for the purpose stated, they have not been

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entirely satisfactory for several reasons among which may be mentioned the relatively high percentage of these salts per weight of the article to be protected which is generally required to give satisfactory results and also the fact that prior pest control agents of this character are not sufficiently resistant to the action of water leaching. Washing of fabrics so treated or the action of rain or snow thereon have been found to materially decrease the effectiveness of the treatment.

A standard test employed to determine the efficiency of toxicant treatments of the character specified is to bury samples of treated material in infected soil for a predetermined period. Chart I, given below, graphically shows a 14 day soil burial test before and after leaching of different fabric specimens, treated with standard water-insoluble metallic salt fungicides. The leaching in these tests is carried out by subjecting 72 square inches of the fabric specimen to 24 hours' leaching at a rate of 8,000 grams of water per hour.

Composition	Percent Fungicide Metal Deposited Per Initial Weight of Cotton Fabric	Percent Tensile Strength Retained (based on initial tensile strength as 100) of fabric when subjected without leaching to soil burial test	Percent Tensile Strength Retained (based on initial tensile strength as 100) of fabric when subjected after water leaching to soil burial test
Commercial grade of copper naphthenate solution containing 8% copper	0.5	90	45
Commercial grade of zinc naphthenate solution containing 8% zinc	1.0	85	43
Commercial grade of copper oleate solution containing 6% copper	0.5	75	40
Commercial grade of cadmium naphthenate solution containing 8% cadmium	1.2	80	45
Commercial grade of copper tallate solution containing 6% copper	0.5	72	39

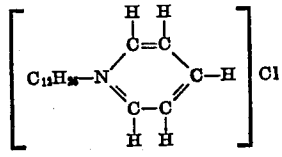
From the foregoing, it is apparent that the efficiencies of the several fungicides tested are very materially affected by water leaching and also that the microbial organisms have a very serious degrading effect upon the strength of the fabric.

The foregoing chart likewise shows that the protective action of the tested agents are highly effective, when judged according to present day standards. It is, however, desirable to increase their efficiency so that the treated articles may be more effectually and permanently protected against the action of the various inimical organisms involved.

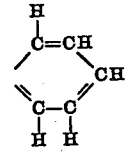
With full knowledge of the shortcomings of these biological control agents referred to above, a great deal of research work was carried out in an effort to overcome these defects. It was discovered, as a result of protracted studies and experimentation, that it is possible to so modify these agents as to render them far better in every respect and every purpose for which they are intended. I have discovered in particular that the addition of minor ratios of quaternary ammonium compounds will produce these improvements. By quaternary ammonium compounds, I means substituted ammonium salts of the general formula:



wherein: R_1, R_2, R_3 and R_4 are organic radicals, either aliphatic, alicylic, aromatic, or heterocyclic and may be substituted or unsubstituted. The four radicals R_1, R_2, R_3 and R_4 may be identical as in tetramethyl ammonium bromide, or completely dissimilar, as in cetylethylmethylbenzyl ammonium chloride. In addition, two or three of the radicals, R_1, R_2, R_3 and R_4, may be replaced by a ring structure of equivalent valence as in lauryl pyridinium chloride



where three groups are replaced by the tri-valent ring structure



X in said formula is an anion, such as Cl,

HSO_4, CH_3COO, etc., derived from a water-soluble acid, inorganic or organic, such as HCl, HI, H_2SO_4, H_3PO_4, HBr, HF, H_2SiF_6, HNO_3, CH_3COOH, CH_3CH_2OH COOH,

(COOH—CH_2—C(OH) (COOH)—CH_2—COOH)

C_6H_4(OH) (COOH), etc.

It thus appears that this invention employs, generally speaking, quaternary ammonium compounds wherein four valences of the nitrogen atom are linked to organic radicals and the fifth valence is linked to an anion of a water-soluble acid.

Among the quaternary ammonium compounds which I have employed in the carrying out of my invention are:

Dodecyldiethylfurfuryl ammonium iodide
Dimethylphenyl (sulphobenzyl) ammonium sulfate, dodecyl ester
Cyclohexyldodecyldimethyl ammonium bromide
(2-hydroxypropyl) trimethyl ammonium iodide
Trimethyl (2-hydroxyphenyl) trimethyl ammonium iodide
Didodecyldimethyl ammonium chloride
(2-bromoethyl) trimethyl ammonium bromide
(5-tert-amyl-2-hydroxyphenyl) trimethyl ammonium iodide
(α-Amino-p-tolyl trimethyl ammonium chloride
Lauryl pyridinium chloride
Dodecyldimethylbenzylammonium chloride
9-octadecenyldimethylbenzyl ammonium bromide
Cetyldimethylbenzyl ammonium lactate
Dodecyldimethyl-o-chlorbenzyl ammonium chloride
p-Tert - octylphenoxyethoxyethyldimethylbenzyl ammonium chloride
Di - isobutylphenoxyethoxyethyldimethylbenzyl ammonium citrate
Di - isobutyloresoxyethoxyethyldimethylbenzyl ammonium chloride
Beta-acetoxyethylcetyldimethyl ammonium p-hydroxy-benzoate
Carbethoxymethyldimethyllauryl ammonium salicylate

The quaternary ammonium compounds which I have found particularly advantageous for this purpose are in themselves water-soluble (this applies to all of the enumerated quaternary ammonium compounds). Thus it could not be foreseen, even by those skilled in the art, that the addition of minor proportions of these quaternary ammonium compounds to substantially water-insoluble salts of naphthenic acids and other organic water-insoluble acids would improve the resistance of these salts to the effects of water leaching. As far as the percentages of these quaternary ammonium compounds are concerned, I have found that they are useful in ratios as low as .05% and as high as 25% per weight of the metal salt.

The tests made on this invention have brought out the wholly unpredictable and remarkable fact that the presence of these substantially water-soluble quaternary ammonium compounds not only increases the resistance to water leaching of the toxicant metallic salts, but they also greatly improve the fungicidal performance or efficacy of the resulting composition.

The following examples are illustrative of the present invention and appended to these examples is a Chart II, wherein the effect of the addition of the quaternary ammonium salts to

standard water-insoluble metallic salt fungicides, as set forth in certain of these examples, is compared with material treated with commercial grades of fungicidal agents in which the quaternary ammonium salts are not present.

EXAMPLES

Example 1

This material is used as a control in our fungicide tests and consists of a commercial grade of copper naphthenate solution containing 8% copper as metal. This material heretofore has been among the most prominent of agents particularly useful as a fungicide for the treatment of cellulosic articles and the like.

Example 2

To 100 grams of a commercial grade of copper naphthenate solution containing 8% copper as metal is added, with vigorous agitation, 2 grams of a 50% solution of lauryl pyridinium chloride. Agitation is continued for ½ hour when a homogeneous solution is obtained. The end product of this example has been checked in practical field tests and has been found to possess greatly superior performance as compared with the straight copper naphthenate solution. It has much better protection against the effect of weathering, including rain, to such cellulosic articles as awnings and sandbags. It has also shown great promise as a fungicide for agricultural purposes.

Example 3

To 100 grams of a commercial grade of copper naphetenate solution containing 8% copper as metal is added, with vigorous agitation, 1 gram of a 50% solution (in monoethylether of ethylene glycol) of dodecyldimethylbenzyl ammonium chloride. Agitation is continued until a homogeneous solution is obtained. The end product of this example has been checked and has been proven as a very excellent pest control agent.

Example 4

To 100 grams of a commercial grade of copper naphthenate solution containing 8% copper as metal is added, with vigorous agitation, 1.5 grams of 9-octadecenyldimethylbenzyl ammonium bromide. Agitation is continued until a homogeneous solution is obtained. The end product of this example shows excellent effectiveness as an insecticide and fungicide.

Example 5

To 100 grams of a commercial grade of copper naphthenate solution containing 8% copper as metal is added, with vigorous agitation, 4 grams of cetyldimethylbenzyl ammonium chloride. Agitation is continued until a homogeneous solution is obtained. The end product of this example has been thoroughly investigated and found to be a superior agent for the control of micro-organisms and insects.

Example 6

To 100 grams of a commercial grade of copper naphthenate solution containing 8% copper as metal is added, with vigorous agitation, 2 grams of dodecyldimethyl - o - chlorbenzyl ammonium chloride. Agitation is continued until a homogeneous solution is obtained. The end product

of this example has shown itself to be an excellent pest control agent for many applications.

Example 7

To 100 grams of a commercial grade of zinc naphthenate solution containing 10% zinc as metal is added, with vigorous agitation, 1 gram of a 50% monoethyl ether of ethylene glycol solution of lauryl pyridinium chloride. A homogeneous solution is obtained. This end product shows great advantage over the performance of the unmodified zinc naphthenate.

Example 8

To 100 grams of a commercial grade of zinc naphthenate solution containing 10% zinc as metal is added, with vigorous agitation, 5 grams of cetyldimethylbenzyl ammonium iodide. A homogeneous solution is obtained. The end product of this example has been thoroughly checked and has proved itself to be an outstanding pest control agent.

Example 9

To 100 grams of a commercial grade of zinc naphthenate solution containing 8% zinc as metal was added, with vigorous agitation, 4 grams of a 25% alcohol solution of cetyl trimethyl ammonium bromide. A clear homogeneous solution was obtained. The end product of this example is an excellent pest control agent, particularly for the protection of wood.

Example 10

To 100 grams of a commercial grade of copper oleate solution containing 6% copper as metal was added, with vigorous agitation, 3 grams of a 30% solution of lauryl pyridinium chloride in ethyl alcohol. A homogeneous solution was obtained. The end product of this example has proved itself as an outstanding fungicide and insecticide.

Example 11

To 100 grams of a commercial grade of copper tallate solution containing 6% copper as metal was added, with vigorous stirring, 2 grams of cetyl dimethyl ethyl ammonium bromide. The temperature of the mixture was raised to 180° F. while stirring. A homogeneous solution was obtained. The end product of this example is an excellent pest control agent, particularly as an ingredient of anti-fouling paints.

Example 12

To 100 grams of a commercial grade of zinc naphthenate containing 12% zinc as metal is added, with agitation, 50 grams of a 50% monoethyl ether of ethylene glycol solution of lauryl pyridinium chloride. The product, containing 6.6% zinc and 16% of the lauryl pyridinium chloride is a clear homogeneous liquid. The end product of this example is an excellent pest control agent, particularly for the protection of wood.

Example 13

To 100 grams of a commercial grade of copper naphthenate emulsion base containing 8% copper is added 60 grams of a 60% monoethyl ether of ethylene glycol solution of dodecyldimethyl benzyl ammonium chloride. The product is a homogeneous liquid containing 5% copper and 22.5% of dodecyldimethyl benzyl ammonium chloride. The end product of this example has proven itself as an excellent fungicide and insecticide.

Example 14

To 100 grams of a commercial grade of zinc naphthenate solution containing 8% zinc is added 33 grams of lauryl pyridinium chloride. The mixture is agitated for 1 hour at 180° F. The product is a homogeneous liquid containing 6% zinc and 25% lauryl pyridinium chloride. The end product of this example is an excellent pest control agent, particularly as an ingredient of anti-fouling paints.

Example 15

To 100 grams of a commercial grade of a solution of the copper salt of a petroleum sulfonate containing 3% copper was added .5 gram of a 50% solution of p-tert-octylphenoxyethoxyethyl dimethyl benzyl ammonium chloride in monoethyl ether of ethylene glycol. The mixture was agitated for ½ hour. The product was a homogeneous solution containing 3% copper as metal. The end product of this example has been investigated and found to be a superior agent for the control of micro-organisms and insects.

Example 16

To 100 grams of a commercial grade of copper 2-ethylhexoate solution containing 4% copper as metal was added 5 grams of a 50% solution of cetyldimethylbenzyl ammonium chloride in monoethyl ether of ethylene glycol. The mixture is agitated for ½ hour. The product is a homogeneous solution. The end product of this example has been checked and has been proven as a very excellent pest control agent.

Example 17

To 100 grams of a solution of zinc naphthenate and iron naphthenate in toluene containing 4% zinc and 1% iron was added two grams of dodecyldimethyl benzyl ammonium chloride. The mixture was agitated for ½ hour at 160° F. and yielded a homogeneous solution. The end product of this example shows considerably better performance than the unmodified combination of the two salts, particularly in the field of wood preservation.

Example 18

To 100 grams of a commercial grade of copper naphthenate solution containing 6% copper was added 1 gram of terbutyl phenoxyethoxyethyl dimethylbenzyl ammonium chloride and 1 gram of lauryl pyridinium chloride. The mixture was agitated for ½ hour at 160° F. and yielded a homogeneous solution. The end product of this example is an excellent pest control agent, particularly for the protection of wood.

Example 19

To 100 grams of a commercial grade of zinc naphthalenate solution containing 8% zinc was added 16 grams of a 50% solution of lauryl pyridinium chloride in monoethyl ether of ethylene glycol, and 7 grams of a 50% isopropyl alcohol solution of dodecyldimethyl benzylammonium chloride. The mixture was agitated for ½ hour at room temperature. The product was a clear homogeneous solution containing 6% zinc and 12.5% mixed quaternary ammonium compound. The end product of this solution is an excellent pest control agent, particularly as an ingredient of anti-fouling paints.

Example 20

To 100 grams of a commercial grade of copper naphthenate solution containing 8% copper as metal is added, with vigorous agitation .05 gram of dodecyldimethylbenzyl ammonium chloride. Agitation is continued until a homogeneous solution is obtained. The end product of this example has shown itself to be an excellent pest control agent for many applications.

Example 21

To 100 grams of cadmium naphthenate containing 8% cadmium was added 4 grams of a 50% solution of lauryl pyridinium chloride in monoethyl ether of ethylene glycol. The mixture was agitated until a homogeneous solution resulted. The end product of this example is an excellent pest control agent, particularly for the protection of wood.

Example 22

To 100 grams of a xylol solution containing 4% cadmium as cadmium naphthenate and 4% cadmium as cadmium 2-ethylhexoate was added 2 grams of cetyldimethylbenzyl ammonium chloride. The mixture was agitated for ½ hour at 180° F. The product was a clear homogeneous solution. The end product of this example has proven itself an excellent pest control agent, particularly for the protection of wood.

Example 23

To 100 grams of a commercial grade of chromium naphthenate solution containing 4% chromium was added 1 gram of lauryl pyridinium chloride. The mixture was agitated until a homogeneous solution resulted. The end product of this example is superior to the unmodified chromium naphthenate, particularly as a wood preservative.

Example 24

To 100 grams of xylol solution of barium naphthenate was added 4 grams of a 50% solution of lauryl pyridium chloride in monoethyl ether of ethylene glycol. The mixture was agitated for ½ hour. The product was a homogeneous solution. The end product of this example proved itself as an excellent fungicide and insecticide.

Example 25

To 100 grams of solid copper oleate containing 10% copper metal and maintained at a temperature of 190° F. was added 2 grams of a 50% solution of lauryl pyridinium chloride in monoethyl ether of ethylene glycol. The mixture was agitated for 1 hour at 190–200° F. and allowed to cool. The product was a soft waxy solid, homogeneous in character, containing 9.5% copper metal and 2% of a quaternary ammonium compound. The end product of this example is an excellent pest control agent, particularly as an ingredient of anti-fouling paints.

Example 26

To 100 grams benzene solution of copper stearate containing 1% copper metal and maintained at a temperature of 150° F. was added 1 gram of a 50% monoethyl ether of ethylene glycol solution of lauryl pyridinium chloride. Upon agitation, the resulting solution was clear and homogeneous. The end product of this example is an excellent pest control agent, particularly for the protection of wood.

Chart II, hereinbefore referred to, follows:

Chart II. Effect of addition of quaternary ammonium salts to standard water-insoluble metallic salt fungicides

[In this chart is given the performance in the standard 14 day soil burial test before leaching, as well as after the fabrics have been subjected to a leach test of 24 hours at the rate of 8,000 grams of water per each hour. There is also shown on a few of the fabrics the relative performance of them (unleached) after a four weeks' soil burial test. Furthermore, there is also shown the visual appearance of the various treated fabrics after the soil burial test.]

Composition	Percent Fungicide Metal Deposited Per Initial Weight of Cotton Fabric	Visual Appearance of Fabric after 14 days' soil burial test		Percent Tensile Strength Retained (based on initial tensile strength as 100) of fabric when subjected to soil burial test		Percent Tensile Strength Retained (based on initial tensile strength of 100) of unleached fabric after 4 weeks in soil burial test
		Leached	Unleached	Leached	Unleached	
Commercial grade of copper naphthenate solution containing 8% copper.	0.5	considerable staining evident due to microbial activity.	normal, no evidence of staining due to microbial activity.	45	90	8
Composition described under Example 2.	0.5	normal, no evidence of stain due to microbial activity.	normal, no evidence of staining due to microbial activity.	81	100	----------
Composition described under Example 3.	0.5	----do----------	----do----------	94	100	----------
Commercial grade of copper oleate solution containing 6% copper.	0.5	heavy staining due to microbial activity.	slight evidence of staining due to microbial activity.	40	75	----------
Composition described under Example 10.	0.5	normal, no evidence of staining due to microbial activity.	normal, no evidence of staining due to microbial activity.	92	95	----------
Commercial grade of zinc naphthenate solution containing 8% zinc.	1.0	heavy staining due to microbial activity.	normal, no evidence of staining due to microbial activity.	43	85	18
Composition as described under Example 7.	1.0	normal, no evidence of staining due to microbial activity.	normal, no evidence of staining due to microbial activity.	75	95	49
Commercial grade of cadmium naphthenate solution containing 8% cadmium.	1.2	considerable staining evident due to microbial activity.	normal, no evidence of staining due to microbial activity.	45	80	----------
Composition as described under Example 22.	1.2	normal, no evidence of staining due to microbial activity.	normal, no evidence of staining due to microbial activity.	80	94	----------
Composition as described under Example 5.	0.5	----------	normal, no evidence of staining due to microbial activity.	----------	100	89

The foregoing Chart II shows very clearly the remarkable results accomplished by the present invention from the standpoints of stabilizing or making permanent the toxicant treatment against water leaching, the increased efficiency of the toxicants, as such, both before and after leaching, and the relatively little loss of tensile strength which the present invention insures.

It will of course be understood that Chart II primarily involves tests upon treated cellulosic fabric wherein changes in tensile strength of the fabric are an important criteria. In other cellulosic articles of commerce generally and economic crops, the degree of resistance of pest attack may be measured by other criteria than tensile strength, but the examples, hereinbefore given, adequately demonstrate that the present invention is highly efficient for these various purposes in the several fields under consideration.

The foregoing description sets forth the invention in preferred practical forms, but the invention is to be understood as fully commensurate with the appended claims.

Having thus fully described the invention, what I claim as new and desire to secure by Letters Patent is:

1. A new composition of matter useful as a pest control agent comprising: a homogeneous solution of at least one substantially water-insoluble copper salt of naphthenic acid and at least one substantially water-soluble quaternary ammonium compound, wherein four valences of the nitrogen are linked to organic radicals and the fifth valence is linked to an anion of a substantially water-soluble acid.

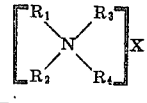
2. A new composition of matter useful as a pest control agent comprising: a homogeneous solution of at least one substantially water-insoluble salt of a mono-basic organic acid and a lesser amount of lauryl pyridinium chloride.

3. A new composition of matter useful as a pest control agent comprising: a homogeneous solution of at least one substantially water-insoluble salt of a mono-basic organic acid and a lesser amount of cetyldimethylbenzyl ammonium lactate.

4. As a new composition of matter a homogeneous solution of a substantially water-insoluble salt of naphthenic acid and lauryl pyridinium chloride.

5. As a new composition of matter a homogeneous solution of a substantially water-insoluble salt of naphthenic acid and cetyldimethylbenzyl ammonium lactate.

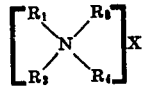
6. As a new composition of matter useful as a pest control agent resistant to water leaching; an oil soluble solution containing at least one substantially water-insoluble metal salt of a mono-basic organic acid stabilized against water leaching by not more than 25% per weight of the metal salt of at least one substantially water-soluble quaternary ammonium compound having the following formula:



wherein R_1, R_2, R_3, and R_4 are organic radicals and X is an anion derived from a substantially water-soluble acid.

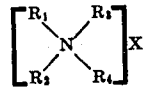
7. As a new composition of matter useful as a pest control agent resistant to water leaching;

an oil soluble solution containing at least one substantially water-insoluble metal salt of naphthenic acid stabilized against water leaching by not more than 25% per weight of the metal salt of at least one substantially water-soluble quaternary ammonium compound having the following formula:



wherein R_1, R_2, R_3, and R_4 are organic radicals and X is an anion derived from a substantially water-soluble acid.

8. As a new composition of matter useful as a pest control agent resistant to water leaching; an oil soluble solution containing at least one substantially water-insoluble zinc salt of naphthenic acid stabilized against water leaching by not more than 25% per weight of the metal salt of at least one substantially water-soluble quaternary ammonium compound having the following formula:



wherein R_1, R_2, R_3, and R_4 are organic radicals and X is in anion derived from a substantially water-soluble acid.

9. As a new composition of matter useful as a pest control agent resistant to water leaching; an oil-soluble solution containing at least one substantially water-insoluble metal salt of a monobasic organic acid stabilized against water leaching by not more than 25% per weight of the metal salt dodecyldimethyl benzyl ammonium chloride.

10. As a new composition of matter useful as a pest control agent resistant to water leaching; an oil-soluble solution containing at least one substantially water-insoluble metal salt of naphthenic acid stabilized against water leaching by not more than 25% per weight of the metal salt dodecyldimethyl benzyl ammonium chloride.

11. As a new composition of matter useful as a pest control agent resistant to water leaching; an oil-soluble solution containing a zinc salt of naphthenic acid stabilized against water leaching by not more than 25% per weight of the metal salt dodecyldimethyl benzyl ammonium chloride.

MILTON GOLL.

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