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CHLORINATED PARAFFIN WAX AMINES FOR CONTROLLING FUNGI AND BACTERIA

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The present invention relates to the control of micro biological pests and pertains particularly to compositions for and methods of preventing fungicidal and bactericidal attack on textiles, such as cotton.

A special problem often encountered is the prevention of disintegration of textiles, especially cotton, due to attack by mould fungi and bacteria. It is particularly difficult to prevent biological decay and loss of strength in textiles that may be exposed to severe weathering, since fungi and bacteria which attack textiles are widely distributed in nature. For example, the most commonly occurring types are species of Aspergillus and Penicillium, together with various Fungi Imperfecti such as Cladosporium and Stemphylium. In the past, in order to prevent decay of textiles, it has generally been necessary to use waterproofing treatments, such as impregnations with bitumens, waxes, rubber compounds, etc. Other treatments, such as with copper naphthenate and other similar materials, have also been proposed. However, these treatments are not fully satisfactory for various reasons, including the shortness of the period of effective prevention, low efficiency, attack of the textiles by the agents themselves, etc.

It is therefore a general object of the present invention to provide more efficient fungicidal and bactericidal compositions.

It is another object of this invention to provide a method of controlling micro biological pests, such as fungi and bacteria.

An object of the invention is to provide a treating composition and method for preventing attack on cellulosic materials and proteins by fungi and bacteria. Specifically, it is an object to protect textiles exposed to severe weathering conditions.

It has now been found that relatively high molecular weight ali chloroamines (including aliphatic and alicyclic, i. e., non-benzenoid chloroamines), and mixtures containing these compounds are highly effective fungicides and bactericides, especially in preventing biological decay and disintegration of textiles exposed to severe weather conditions, particularly under conditions of high moisture, such as burial in or contact with wet soil. Such compounds contain at least 12, and preferably 20–40, or more carbon atoms; preferably two olefinic double bonds; at least one, preferably two or more amino groups; and at least one non-ionizable chlorine atom. It is further desirable that the compound contain an oleophilic hydrocarbon radical of 8 carbon

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atoms or more, this radical preferably being unsaturated and attached to an amino group. The amino groups may be primary, secondary and tertiary, and are preferably attached to other than terminal carbon atoms. The compounds may also contain other inorganic substituents, such as hydroxy, cyano, thiocyano, nitro, carbonyl, ether, thioether, mercapto, etc. The present agents may be used as the free base.

As examples of suitable higher molecular weight unsaturated ali chloroamines, the following may be mentioned: chloro amino cetane, chloro amino hexadecane, diamino chloro cetene, diamino chloro eicosene; di(N-dimethyl amino) chloro octadecene; triamino ethyl methyl chloroisopropyl dedecene; diamino chloromethyl isobutyl methyl cetene; diamino chloro triacontylene; N-ethyl methyl chlorohexyl amino propyl cyclohexenylamine; chloro amino tetra-iso-butylene, etc.

Suitable mixtures of compounds may be obtained by incomplete ammonolysis of chlorinated hydrocarbons of at least 12 carbon atoms and more than 2, and preferably 3 or more, chlorine atoms. Suitable hydrocarbons include, for example, hard and soft paraffin wax, Vaseline, transformer oil, various lubricating oils and other mineral oils having more than about 12 carbon atoms. Paraffinic or naphthenic oils or both are suitable and their aromatic content should preferably be relatively low.

An especially effective agent is obtained from paraffin wax by chlorination and ammonolysis, the former reaction being conducted at a temperature of about 105° C. to 125° C. until a chlorine content of about 15%, and preferably about 25–38%, is reached; and the latter reaction taking place at about 150° C. to 175° C. under an ammonia gas pressure of about 300–500 pounds per square inch in the presence of a solvent such as ethyl alcohol. The resulting product normally has a molecular weight range of 450–600, contains per molecule 1.2–2.5 amino groups of which about 75% are primary and secondary and the remainder tertiary amino groups, 1–2 olefinic double bonds, and about 0.5–1.5 non-ionizable chlorine atoms. It is obtained at about a 50–50 mixture of the free base and the hydrochloride salt of the latter. In the following description such a free base or the like will be referred to as "chlorinated paraffin wax amines," or "wax amines" for short. A more detailed description of a method for preparing the present wax amines will aid in practicing the present invention, which method is as follows: a paraffinic

rbon comprising a large proportion of zable components is chlorinated in the hase at a temperature of 100° C.–125° C. chlorine content above 15% is reached. orinated product is ammonolyzed, pref- ı the presence of a solvent, at a tempera- ›ve 140° C. and the amines thus formed .rated. The hydrocarbon material should molecular weight above 250 and prefer- ween 350 and about 800 and should con- substantial proportion of crystallizable s. The nature of the hydrocarbons de- s to a large extent the properties of the produced by this process. If a hydrocar- taining less than 90% of crystallizable s is used, it is often advantageous to sub- rior to chlorination to a de-oiling opera- h as sweating, crystallization from a sol- paration with the aid of a dewaxing sol- h as propane or a mixture of dimethyl or acetone with benzol or toluene, etc., to increase the concentration of crys- e components. The properly selected hy- on material is chlorinated with gaseous without the use of special catalysts under ns insuring thorough and uniform contact for example, bubbling the gas into the ıydrocarbon through a porous plate, and gitation of the reaction mixture. The n may be conducted under moderate mospheric pressures in an autoclave, but ferred to effect it in a vessel maintained ıbstantially atmospheric pressure. After tion is completed, it is advantageous to reaction mixture of dissolved chlorine ochloric acid, for example, by applying or passing therethrough an inert gas such ocarbon gas, carbon dioxide, hydrogen, , etc. If this step is omitted, part of the a employed in the following operation is ly neutralized or oxidized. The chlorin- lrocarbon is then dissolved in a suitable preferably methyl or ethyl alcohol; the solution is treated with ammonia under at elevated temperature. Suitable sol- ust possess solvent power for both the ed hydrocarbon and ammonia and must ically inert under conditions of ammo- Water-soluble ethers, alcohols such as lycerol, propanol, tertiary butanol, sec- pentanol, dimethyl, di-ethyl, methyl- ethyl-propyl ether, mono- or di-methyl her, mono-, di- or tri-methyl glycerol -ethylene dioxide, etc., and particularly nd ethyl alcohol are among the suitable If desired, they may contain up to about er. The commercial azeotrope of ethyl nd water, containing about 5% of water, st practical solvent due to its availability of recovery. At room temperature chlo- vax is but little soluble therein but at ures above about 120° C. it dissolves wo to five volumes of the solvent are in sufficient. Ammonolysis is preferably d in an autoclave allowing moderate f the reacting mixture, particularly at ning of the reaction to produce uniform The necessary quantity of ammonia is at least 1–2 equivalents of the chlorine f the hydrocarbon. In order that the may proceed at a reasonable speed and ntial completion, it is desirable that the ressure of ammonia be maintained at 00 p. s. i. and preferably from 150 to 200 ring the entire time, i. e. until the am-

monolysis is completed. Thus, for example, 8%–10% of ammonia may be dissolved in the solvent prior to the introduction of the chlorinated hydrocarbon or, if desired, the solution of chlorinated hydrocarbon in the solvent is first brought to the reaction temperature and the amount of ammonia necessary to produce the desired increase in pressure is thereafter introduced. Ammonolysis may be carried out at temperatures between about 135° C. and 200° C. At temperatures below 140° C. the ammonolysis proceeds very slowly. At temperatures above about 175° C. it proceeds very rapidly but the amines obtained do not possess as good bonding properties. Thus temperatures from 140 C. to 175° C. and particularly from 150° C. to 160° C. are preferred for best results. Ammonolysis is continued at least until substantially complete, i. e. until it does not proceed further at an appreciable rate and most of the chlorine combined with the hydrocarbon has been displaced, but may be continued if convenient for longer periods up to 10–15 hours; 3–6 hours, in general, suffice. If desired, soaking at the reaction temperature may advantageously be prolonged, i. e., may be continued for 10–15 hours. The resulting product contains amines thus formed, excess ammonia, the solvent and ammonium chloride, the latter being largely insoluble in the mixture. Part of the amines are free, and the other part in the form of hydrochloride salts. After completion of ammonolysis, the crystals of ammonium chloride are separated as by conventional filtration, and if desired the ammonia together with the solvent may be recovered from the filtrate by distillation for further use in the process. The amines thus separated are obtained in partially neutralized form. Free amines or different salts may be prepared therefrom by conventional methods.

Although the unsaturated chloro-containing polyamine mixtures are preferred, many other groups of polyamines may be used, among which are the alpha branched aliphatic primary polyamines, having more than 12 carbon atoms, which are derived from aliphatic mono-olefins by hydrochlorination and ammonolysis, and may be referred to as "alpha methyl amines" or "alpha amines."

In some cases, mixtures of compounds containing among them the essential groups may be used. Thus, there may be used a mixture of compounds containing per average molecule more than one amino group, more than one double bond, 0.5 to 1.5 non-ionizable chlorine atoms, and an oleophilic hydrocarbon chain of at least 8 carbon atoms linked to an amino group. For example, there may be mentioned mixtures of higher molecular weight aliphatic polyamines having an oleophilic hydrocarbon chain of at least 8 carbon atoms and unsaturated aliphatic chlorides.

For use in treating textiles, according to the preferred application of the agents of the present invention, volatile and readily vaporizable solvents may be used as carriers for said agents. Suitable carriers include, for example, aliphatic, araliphatic, and aromatic organic solvents, such as mineral or petroleum spirits, carbon tetrachloride, ethylene dichloride, dichloro diethyl ether, di-isopropyl ether, petroleum ether, naphtha, kerosene, ethylene glycol, benzene, toluene, alcohols, acetone, mixtures thereof and the like, aqueous solutions or suspensions, etc. Aside from readily vaporizable solvents, materials such as viscous oils, various polymers and plastic resins, creosote oils, water-proofing emulsions such as of

aluminum acetate, soap, and wax, etc. may also be used as carriers for the present agents. Generally about 5–35% of the present agents are dissolved or suspended in the carrier, although more or less may be used, depending on the character of the carrier and agent used. Other agents, toxic or otherwise, may also be incorporated in the carrier. For example, insect repellents or insecticides, such as dichloro diphenyl trichloro ethane, phenothiazine, etc., emulsifiers, coloring agents, perfumes, etc., may be added to the carrier.

In treating textiles, such as cotton, linen, jute, bagasse and the like, including keratinous textiles and fabrics, such as wool, the present agents may be applied thereto by dipping, spraying, or brushing with solutions of the agents, preferably in a volatile solvent, such as benzene. As a rule, at least 2 or 3% and generally more than 10% by weight (on the basis of treated cloth) of the agents are applied to the cloth. Preferred is the impregnation of the textile with 15% to 30% or more of the present agents, such as the wax amines.

After the textiles have been treated with the present agents, they may be subsequently treated with other agents for various purposes. For example, a chloro polyamine treated fabric or mesh may be impregnated with bituminous material in forming a reinforced asphaltic revetment lining.

The present method of preventing attack on textiles by fungi and bacteria may be applied to fish-nets, canvas-goods, such as tents, awnings, ground-sealing covers, etc., burley sacks used for sand-bags, fabrics used in reinforcing revetment linings of asphalt and the like, etc.

The agents of this invention together with certain similar but ineffective agents were tested for prevention of attack by fungi and bacteria on heavy cotton canvas under severe weathering conditions in the following manner. Canvas swatches were impregnated with the cloth preservatives and duplicate samples buried in garden loam maintained moist at 90° F. At the end of 3 months for one series and 6 months for another series the soil was carefully removed and the condition of the cloth determined. The results of these tests are shown in the following table:

Preservative	Per Cent Preservative (based on wt. of treated cloth)	Length of Test Period	Condition of Cloth Swatch
		Mos.	
None	None	6	Completely disintegrated.
Zinc naphthenate	17.1; 20.4	6	Do.
Creosote	43.9; 43.2	6	Do.
Asphalt	56.2; 54.0	6	Partially disintegrated; no tensile strength.
Asphalt cutback (RC)	50.8; 53.4	6	Do.
Do	45.5; 45.3	6	Do.
Chlorinated paraffin wax amines (free base)	26.8; 25.8	6	Unaffected.
n-Octadecylamine	17.0; 18.1	6	Cloth completely disintegrated.
Lauryl-pyridinium-bromide	3.0	6	Do.
None	None	6	Do.
Asphalt cutback (RC) containing 3% wax amine.	43.0	6	Cloth very weak but not disintegrated.

It will be seen from the data that wax amines, in the form of the free bases, are surprisingly superior to other cloth preservatives, the canvas swatches treated therewith being virtually unaffected by the severe conditions of the burial. In fact, the tensile strength of a wax amine treated sample remained substantially the same. For example, the tensile strengths of a ¾ inch wide canvas swatch after various treatments were as follows: untreated—75 lbs., after treatment with about 22% wax amine—85 lbs., and after 3 months burial of the treated sample—86 lbs.

Besides being useful as a toxicant or repellent in textile preserving compositions, these chloro polyamines may also be used to control various organisms, particularly fungi and bacteria, in wood, soil, plants, seeds, etc. For use in wood preservatives, the present agents may be dissolved or suspended in preferably clear petroleum oils, cresylic acids (i. e. alkyl phenols which may boil between about 200–350° C.), volatile organic solvents, aqueous solutions, etc. with or without the addition of other wood preservatives and applied to wood by impregnation, spraying, brushing, etc.

For agricultural use on and in soils, the agents may be incorporated in a volatile organic solvent, aqueous liquid, etc. with or without the addition of other soil treating agents, such as soil fumigants, e. g. lower unsaturated polychlorides of the allyl-vinyl type, mixtures of saturated and unsaturated polychloro hydrocarbons of 3 to 4 carbon atoms, etc., or such as fertilizers, e. g. liquid or gaseous ammonia, etc., and applied to the soil by spraying on the surface, injecting below the surface, or distributing with irrigation water.

For use on plants, the present agents may be dissolved or suspended in plant mineral spray oils and emulsified in water to produce sprayable emulsions, or the agents without oil may be emulsified or suspended in water to produce plant sprays. Any suitable emulsifying agent, such as partial esters of polyhydric alcohols, e. g. glycerol mono-oleate, polyethylene glycol mono laurate, palmitate, stearate, oleate, etc., various soaps, alkali metal salts of sulfuric acid mono esters and organic sulfuric acids and the like, may be used in combination with such sprays. In general, the emulsifying agents are used in sufficient amount to resist for a suitable period the tendency of some of the present agents to reverse the emulsions. Likewise, some of the present agents are sufficiently surface-active so that the agents themselves will act as the emulsifier, thereby avoiding the necessity of using a separate emulsifier. If desired, the present agents may also be absorbed on finely-divided solid materials, such as wood flour, talc, clay, sulfur, carbon black, etc., to be used as fungicidal dusts.

Besides being useful in themselves as a toxicant or repellent, the compounds of the present invention may be used in conjunction with well-known insecticides and fungicides. Thus, they may also be used in combination with rotenone, pyrethrum, lead arsenate, nicotine, thiocyanates, copper naphthenate, unsaturated cyclic ketols, such as di-isophorone, dichloro diphenyl trichloro ethane and the like.

I claim as my invention:

1. A method of controlling fungi and bacteria comprising exposing them to mixtures of aliphatic compounds having at least 12 carbon atoms and not more than about 40 carbon atoms and containing per average molecule more than one amino group, at least one olefinic double bond, combined chlorine only in the form of 0.5 to 1.5 non-ionizable chlorine atoms, and an oleophilic hydrocarbon chain of at least 8 carbon atoms linked in an amino group.

2. A method of controlling fungi and bacteria in their attack on cellulosic and protein materials which comprises applying to said materials at least 2% by weight of paraffin wax amines containing per average molecule more than one amino group, at least one olefinic double bond, 0.5 to 1.5 combined chlorine atoms only in the form of non-ionizable chlorine atoms, and a molecular weight from 450 to 600.

3. A method of controlling fungi and bacteria comprising exposing them to mixtures of aliphatic compounds having at least 12 carbon atoms and not more than about 40 carbon atoms and containing per average molecule more than one amino group, at least one olefinic double bond, and combined chlorine only in the form of from 0.5 to 1.5 non-ionizable chlorine atoms.

4. A method of controlling fungi and bacteria comprising exposing them to mixtures of aliphatic compounds containing per average molecule more than one amino group, at least one olefinic double bond, combined chlorine only in the form of from 0.5 to 1.5 non-ionizable chlorine atoms, and a molecular weight from 450 to 600.

5. A method of controlling fungi and bacteria in their attack on textile materials which comprises applying to said materials at least 2% by weight of a mixture of aliphatic compounds having at least 12 carbon atoms and not more than about 40 carbon atoms and containing per average molecule more than one amino group, at least one olefinic double bond, and combined chlorine only in the form of from 0.5 to 1.5 non-ionizable chlorine atoms.

6. A textile article comprising in combination a textile substantially uniformly impregnated with at least 2% by weight of a mixture of aliphatic compounds having at least 12 carbon atoms and not more than about 40 carbon atoms and containing per average molecule more than one amino group, at least one olefinic double bond, and from 0.5 to 1.5 combined chlorine atoms only in the form of non-ionizable chlorine atoms.

7. A textile article comprising in combination a textile substantially uniformly impregnated with at least 2% by weight of chlorinated paraffin wax amines containing per average molecule more than one amino group, at least one olefinic double bond, 0.5 to 1.5 combined chlorine atoms only in the form of non-ionizable chlorine atoms, and a molecular weight from 450 to 600.

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