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OIL-SOLUBLE COPPER-NICOTINE COMPOUNDS AND PROCESS OF PREPARING SAME

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to me of any royalty thereon.

This invention relates to copper-nicotine compounds, and has among its objects the production of such compounds, which are soluble in hydrocarbon oils of petroleum but not in water, and the production of hydrocarbon oil solutions of such compounds for use as insecticides.

The hydrocarbon oils of petroleum are widely used in the destruction of harmful insects. Varying conditions require different grades of the oils, based upon volatility, viscosity, degree of refinement, and so forth, but the toxicity of the oil to the ova, larvae, and adults of many insects, when in the concentrations tolerated by the host, is often insufficient for effective insect control.

Attempts have frequently been made to increase the toxicity of the oil by dissolving other toxic ingredients therein. Compounds of nicotine have been recognized as desirable for this purpose, but heretofore satisfactory nicotine compounds have not been available. The known compounds although soluble in the oil are also soluble in water, rendering them unsuitable.

For example nicotine, if free from water, and a number of its derivative compounds, such as its simple salts with some members of the fatty acids, naphthenic acid, and so forth, can be dissolved in a dry hydrocarbon oil, but when these solutions are brought into contact with water, the nicotine or its salts largely pass from the oil into solution in the water.

I have found that certain members of the soap-forming acids can be formed into their normal cupric salts and then reacted with nicotine by mixing the nicotine and normal cupric salts together to form copper-nicotine compounds soluble in hydrocarbon oil, but not soluble in water, thus resulting in nicotine compounds eminently suitable for the purposes mentioned above.

By soap-forming acids is meant those acids as herein used that form sodium or potassium salts with the property of binding water into a gelatinous mass, commonly referred to as "soap." For example, the saturated aliphatic monocarboxylic acids having from 6 to 14 carbon atoms, inclusive are such soap-forming acids. The saturated aliphatic monocarboxylic acids below hexanoic are not soap-forming acids, and their normal cupric salts, when treated with nicotine,

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form cupric hydroxide and the nicotine salt of the acid, both of which are insoluble in oil in the presence of water, whereas the normal cupric salts of the soap-forming acids used in this invention react with nicotine without decomposition to form copper-nicotine compounds which are soluble in oil and not in water. It is to be understood that use of an excess of nicotine in producing the copper-nicotine compounds from the normal cupric salts may cause decomposition, even with the cupric salts of the soap-forming acids; hence, the amount of nicotine used should generally be limited to the proportion of not substantially more than one molecule of nicotine for each molecule of the cupric salt, although nicotine in an amount up to 1½ molecules may be used.

Other soap-forming acids suitable for use in forming the copper-nicotine compound of this invention include unsaturated aliphatic monocarboxylic acids having from 6 to 18 carbon atoms, inclusive, such as 9-hendecenoic acid, 9-octadecenoic acid (oleic), 9,12,octadecadienoic acid (linoleic), and so forth, whose normal cupric salts are soluble in oil, and abietic acid derived from pine rosin.

Chemically pure soap-forming acids are very expensive, and it is not necessary for the purposes of this invention to employ them. Mixtures of such acids, such as the mixed acids from cocoanut oil, or various fractions derived from mixed acids, may be used. Commercial fatty acids may also be used. However, hexadecanoic (palmitic) and octadecanoic (stearic) acids, if present in substantial amounts in the commercial fatty acids, must be removed at some stage in the preparation of the copper-nicotine compounds, but if their proportions are small, as in some commercial mixed cocoanut oil fatty acids, their removal is not required, probably because the solvent action of the oil-soluble copper-nicotine compounds prevents precipitation of the compounds of the palmitic and stearic acids. Use of commercial oleic acid usually requires a preliminary separation of the oil-soluble fraction from the precipitated cupric salts associated with the water phase.

The process of preparing the new oil-soluble, water-insoluble copper-nicotine compounds involves two essential steps: first, the preparation of the normal cupric salt of the soap-forming acid, and second, the addition of nicotine to the normal cupric salt to form the mononicotine compound of copper.

The normal cupric salt of the soap-forming

acid can be made by the addition of a water solution of a soluble cupric salt, such as cupric acetate or copper sulfate, to a carefully neutralized solution of the sodium salt of the acid. With individual acids or mixtures of acids, the alkali equivalent determines the correct amount of copper required to form the normal cupric salt.

The precipitated normal cupric salt or salts may be converted directly to the copper-nicotine compound or compounds by the addition of 1 to 1½ moles of nicotine per mole of cupric salt dissolved in water and vigorously shaken to effect intimate contact.

The copper-nicotine compound may be extracted from the reaction mass directly by the hydrocarbon oil in which the copper-nicotine compound is to be used, or if a concentrated form of the compound is desired, it may be extracted by some volatile solvent such as petroleum ether or ethyl ether, following which the solvent may be removed by evaporation.

The normal cupric salt of the soap-forming acid often can be conveniently prepared directly in the hydrocarbon oil base in which it is desired to have the copper-nicotine compound dissolved, by first dissolving the soap-forming acid in the oil and thoroughly mixing the solution thus formed with an aqueous solution of the cupric salt of a weak acid such as cupric acetate. Different soap-forming acids vary in the completeness of the change to the cupric salt, partly because of the reverse effect of the liberated acetic acid. However, complete change can be assured by careful neutralization of the acetic acid between intervals of shaking or by discarding the cupric acetate water layer which forms on standing and using additional quantities of the cupric acetate solution. The copper-nicotine compound dissolved in the hydrocarbon oil is then formed by adding nicotine.

Abietic acid when used as the soap-forming acid in the manner mentioned in the first paragraph above does not dissolve readily in hydrocarbon oils, so that the preparation of the normal cupric salt of this acid is preferably carried out in an ether solution. According to this procedure, the acid is combined with the nicotine and ethereal solution and the ether later is removed by evaporation.

Most of the normal cupric salts of the saturated aliphatic monocarboxylic acids are usually only slightly soluble in petroleum oil. Cupric hexanoate is an exception, being quite soluble. The normal cupric salts of the unsaturated fatty acids are generally soluble in the oil, but the normal cupric abietate is only slightly soluble. However, the addition of one molecule of nicotine to each molecule of the cupric salt results in formation of the copper-nicotine compounds from the insoluble cupric salts which are soluble in oil without affecting the solubility of those compounds already dissolved.

The different copper-nicotine compounds derived from different soap-forming acids do not vary substantially in solubility in the petroleum oils, even though oils differing in range of boiling point and viscosity be used, but the more viscous oils require a longer time to complete the solution.

The examples given below serve to illustrate the essential steps in the process of preparing copper-nicotine compounds dissolved in a desired oil base. Commercial methods may vary with the acid or acids to be used, and differ in detail from the convenient procedures indicated.

Example I

One-tenth molar weight of hexanoic acid (11.6 grams) was dissolved in 200 ml. of a refined kerosene oil. One-twentieth molar weight of cupric acetate dihydrate was dissolved in sufficient water and shaken vigorously with the oil solution to form the normal cupric salt in solution in the oil. After standing, the water layer was withdrawn and then two grams of the cupric acetate in water solution was shaken with the oil layer to complete the change of the acid to the normal cupric salt. One-twentieth molar weight of nicotine (8.1 grams) was added directly to the solution of oil and the cupric salt to form the copper-nicotine compound, with a resulting color change from blue to bright green.

Example II

One-tenth molar weight of heptanoic acid (13.0 grams) was dissolved in 200 ml. of a refined kerosene oil. The normal cupric salt was prepared in the oil phase as in Example I, except that several successive portions of cupric acetate solution were required to complete the change to the normal salt. The normal cupric salt was formed partly in solution in the oil but mostly in suspension. The addition of one-twentieth molar weight of nicotine produced a color change similar to that of Example I, resulting from chemical combination of the nicotine and cupric salt followed by solution of the copper-nicotine compound in the oil.

Example III

One-tenth molar weight of octanoic acid (14.4 grams was dissolved in 200 ml. of the refined kerosene oil and treated as in Example II. The cupric salt was formed in suspension in the oil but combined and dissolved on the addition of the nicotine as in Example II.

Example IV

One-tenth molar weight of decanoic acid (17.2 grams) was dissolved in refined kerosene oil and treated as in Example II. The normal cupric salt was formed in suspension in the oil but combined and dissolved on addition of the nicotine and gave the characteristic bright green solution.

Example V

One-tenth molar weight of dodecanoic acid (20.0 grams) was dissolved in 200 ml. of the refined kerosene oil and treated as in Example II. The normal cupric salt of this acid held the oil in a viscous mass, but the addition of nicotine resulted in combining and complete solution as in other previous examples.

Example VI

One-tenth molar weight of tetradecanoic acid (22.8 grams) was dissolved in 200 ml. of refined kerosene oil. The cupric salt was formed as in Example II, with the resulting formation of a viscous mass as in Example V. The addition of nicotine produced complete solution only on warming. In the cold, some insoluble material was formed, probably indicating the limit of solubility had been passed.

Example VII

One-tenth molar weight of 9-hendecenoic acid was dissolved in 200 ml. of refined kerosene oil and the normal cupric salt formed as in Example II. The normal cupric salt remained dissolved in the oil and was combined and changed to the

characteristic bright green color on addition of nicotine. The substitution of a medium grade summer oil for the kerosene in a parallel experiment gave similar resulting products in all steps of the procedure.

Example VIII

One-tenth molar weight (30.2 grams) of abietic acid (actually a good grade of pine rosin) was dissolved in 100 ml. of ethyl ether. The normal cupric salt was prepared by shaking with cupric acetate solution, as in Example II. One-twentieth molar weight of nicotine (8.1 grams) and 200 ml. of kerosene oil was added to the ethereal solution. The ether was removed by evaporation. Some impurities separated from the oil on standing several days, permitting decantation of the clear, green copper-nicotine compound in oil solution.

Example IX

One-tenth average molar weight of the mixed cocoanut oil fatty acids (20.0 grams) was dissolved in 200 ml. of refined kerosene. The normal cupric salts prepared as in Example II formed a viscous mass with the oil, but the addition of nicotine resulted in formation of the copper-nicotine compounds in complete solution. Parallel experiments in which different grades of hydrocarbon oils were substituted for the kerosene yielded similar results in all respects.

Example X

One-tenth average molar weight of the mixed cocoanut oil fatty acids (20.0 grams) was neutralized with the theoretical quantity of standard sodium hydroxide solution and then precipitated by addition of the theoretical amount of standard cupric acetate solution. The correct amount of nicotine and 200 ml. of kerosene was added and shaken vigorously. On standing, a clear, green solution of the mixed copper nicotine compounds in the oil resulted.

Example XI

One-tenth molar weight of commercial oleic acid (28.4 grams) was neutralized with the theoretical amount of sodium hydroxide solution and 200 ml. of kerosene was added. The equivalent amount of cupric acetate solution was then added slowly while agitating the mixture. After standing for several hours or longer, the oil layer containing the cupric oleate in solution separated from the water layer containing the impurities in suspension. The addition of 8.1 grams of nicotine produced the required chemical combination, with the characteristic color change of the solution without disturbing the solubility in the kerosene.

If concentrated copper-nicotine compounds are desired, they may be prepared by carrying out the essential steps in a suitable volatile solvent, such as petroleum ether, gasoline, ethyl ether, and so forth, rather than in a less volatile petroleum oil, followed by evaporation of the solvent. The desired grade of petroleum oil can be used to dissolve and dilute the concentrated compound.

The copper-nicotine compounds produced according to this invention may be represented by the formula

$$(R—COO)_2Cu.C_{10}H_{14}N_2$$

wherein R is a monovalent saturated aliphatic radical having from 5 to 13 carbon atoms, inclusive, a monovalent unsaturated aliphatic radical having from 5 to 17 carbon atoms, inclusive, or the abietyl radical, and wherein $C_{10}H_{14}N_2$ represents a molecule of nicotine.

Other methods of preparing normal cupric salts of the desired acid or acids and also variation in the order of adding the petroleum oil and nicotine are possible without departing from the essential steps required for the formation of the selected mononicotine compounds of copper.

Having thus described the invention, what is claimed is:

1. A process for the preparation of oil-soluble copper-nicotine compounds comprising reacting nicotine with a normal cupric sale of a soap-forming acid, said acid being selected from the group consisting of the saturated aliphatic monocarboxylic acids having from 6 to 14 carbon atoms, inclusive, the unsaturated aliphatic monocarboxylic acids having from 6 to 18 carbon atoms, inclusive, abietic acid, and a mixture of them, by mixing the nicotine and normal cupric salt together in the proportion of not more than 1½ molecules of nicotine for each molecule of the cupric salt.

2. A process for the preparation of oil-soluble copper-nicotine compounds comprising reacting nicotine with a normal cupric salt of abietic acid by mixing the nicotine and normal cupric salt together in the proportion of not more than 1½ molecules of nicotine for each molecule of the cupric salt.

3. A process for the preparation of oil-soluble copper-nicotine compounds comprising reacting nicotine with a normal cupric salt of a saturated aliphatic monocarboxylic acid having from 6 to 14 carbon atoms, inclusive, by mixing the nicotine and normal cupric salt together in the proportion of not more than 1½ molecules of nicotine for each molecule of the cupric salt.

4. A process for the preparation of oil-soluble copper-nicotine compounds comprising reacting nicotine with a normal cupric salt of an unsaturated aliphatic monocarboxylic acid having from 6 to 18 carbon atoms, inclusive, by mixing the nicotine and normal cupric salt together in the proportion of not more than 1½ molecules of nicotine for each molecule of the cupric salt.

5. A process for the preparation of oil-soluble copper-nicotine compounds comprising reacting nicotine with mixed cupric salts of mixed cocoanut oil acids by mixing the nicotine and cupric salts together in the proportion of not more than 1½ molecules of nicotine for each molecule of the cupric salts.

6. A process of preparing a petroleum hydrocarbon oil solution of copper-nicotine compounds comprising dissolving in the hydrocarbon oil a soap-forming acid, said acid being selected from the group consisting of the saturated aliphatic monocarboxylic acids having from 6 to 14 carbon atoms, inclusive, the unsaturated aliphatic monocarboxylic acids having from 6 to 18 carbon atoms, inclusive, abietic acid, and a mixture of them, forming a normal cupric salt of the soap-forming acid by treating the solution with an aqueous cupric salt, and mixing nicotine therewith in the proportion of substantially one molecule of nicotine for each molecule of the cupric salt.

7. A process of preparing a petroleum hydrocarbon oil solution of a copper-nicotine compound comprising mixing a soap-forming acid, said acid being selected from the group consisting of the saturated aliphatic monocarboxylic acids having from 6 to 14 carbon atoms, inclu-

sive, the unsaturated aliphatic monocarboxylic acids having from 6 to 18 carbon atoms, inclusive, abietic acid, and a mixture of them, an aqueous cupric salt, and nicotine with the petroleum hydrocarbon oil in the proportion of substantially one molecule of nicotine for each molecule of the cupric salt.

8. A process of preparing a copper-nicotine compound comprising mixing a soap-forming acid, said acid being selected from the group consisting of the saturated aliphatic monocarboxylic acids having from 6 to 14 carbon atoms, inclusive, the unsaturated aliphatic monocarboxylic acids having from 6 to 18 carbon atoms, inclusive, abietic acid, and a mixture of them, an aqueous solution of the cupric salt, and nicotine with a volatile solvent, in the proportion of substantially one molecule of nicotine for each molecule of the cupric salt, followed by evaporation of the solvent.

9. A composition of matter represented by the formula

$$(R—COO)_2Cu.C_{10}H_{14}N_2$$

where R is selected from the group consisting of a monovalent saturated aliphatic radical containing from 5 to 13 carbon atoms, inclusive, a monovalent unsaturated aliphatic radical containing from 5 to 17 carbon atoms, inclusive, the abietyl radical, and a mixture of them, and wherein $C_{10}H_{14}N_2$ represents a molecule of nicotine.

10. A composition of matter represented by the formula

$$(R—COO)_2Cu.C_{10}H_{14}N_2$$

where R is a monovalent saturated aliphatic radical containing from 5 to 13 carbon atoms, inclusive, and wherein $C_{10}H_{14}N_2$ represents a molecule of nicotine.

11. A composition of matter represented by the formula

$$(R—COO)_2Cu.C_{10}H_{14}N_2$$

where R is a monovalent unsaturated aliphatic radical containing from 4 to 17 carbon atoms, inclusive, and wherein $C_{10}H_{14}N_2$ represents a molecule of nicotine.

12. A composition of matter represented by the formula

$$(R—COO)_2Cu.C_{10}H_{14}N_2$$

where R is an abietyl radical, and wherein $C_{10}H_{14}N_2$ represents a molecule of nicotine.

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