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DOUBLE SALTS OF NICOTINE

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4 Claims. (Cl. 260—270)

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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 and claimed, 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 is a division of my copending application for patent Serial No. 411,702, filed September 20, 1941, now Patent No. 2,356,185.

The primary object of this invention is the production of new double salts of nicotine which offer resistance to the often undesirable effects of moisture, dew, rain, sun, etc., and can be used effectively against injurious insects upon vegetation.

Many of these new compounds exert a fumigating effect while in the dry dust form superior to any compounds previously known or used. This fumigating effect results from the combinations of nicotine with such volatile acids as benzoic, salicylic, etc. In addition to these advantages, the compounds containing zinc or copper, both of which are components of fungicides, may supply the necessary fungicidal properties in addition to their insecticidal action.

The designation "fixed nicotine compound" has been customarily applied to such weather-resisting materials as the tannate, humate, bentonite, etc., compounds of nicotine. The new compounds of this invention may also be so described but they are quite different in type of chemical composition. In comparison with liquid nicotine and nicotine sulphate, the dry dusts represent more convenient physical forms and many of them possess excellent keeping properties. The natural color of many of the salts afford an additional safety factor against mistaken identification.

Important differences are to be expected in the mode of action of my compounds as compared to nicotine bentonite, which heretofore has been considered to be the most promising of the "fixed nicotine" products. Bentonite releases nicotine only by the hydrolysis and volatilization of the free nicotine, and when the ratio of bentonite to nicotine increases this action is greatly reduced. On dry days, even when hot, very little nicotine will be released. With a number of my new compounds, such as the benzoates and salicylates, the fumigating effect is increased by heat and dryness with simultaneous release of nicotine and the volatile acid. Under moist conditions, a small but definite solubility provides

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nicotine and metal for fungicidal and insecticidal action.

My compounds may be described as "coordinated" or double salts with the metal probably exerting an auxiliary valency toward the nicotine molecule. The nature of the acid is an essential requirement. In the case of most ordinary acids such as boric, oxalic, phosphoric, etc., either they do not serve for double salt formation or no relatively insoluble combinations exist.

The compounds of this invention are limited to the double salts of nicotine with one of the metals iron, zinc, copper, nickel, cobalt and cadmium. They are further limited in the nature of the acid used to bind the nicotine and the metal. The acid is selected from a group of acids consisting of hydrocyanic, thiocyanic, hydroferrocyanic, hydroferricyanic, chromic, benzoic, salicylic, o-benzoyl benzoic and picric acids. The acids containing the —C≡N group are highly susceptible to polymerization and with the metals iron, zinc, copper, nickel, cobalt and cadmium form complex double salts with alkali and alkaline earth metals.

The acids containing the unsaturated benzene ring including benzoic, o-benzoic, o-benzoyl, picric and salicylic acids are also highly effective in double salt formation producing compounds which are generally crystalline and often quite insoluble in water. The cadmium nicotine benzoate, however, is rather soluble and separates only in concentrated solutions. The double chromates are generally fairly soluble and must be prepared from concentrated solutions. The zinc double salt, however, is very insoluble but may be secured in a finely divided crystalline form. The polymerizing tendency of the chromates is seen in the existence of many polychromates such as the dichromates, etc.

There are doubtless many derivatives of benzoic acid other than the ones here employed, such as the 2-4 dichlor, p brom, (their copper salts have been prepared), which will form similar double salts. Orthochlorbenzoic acid, however, cannot be used, because the cost of such derivatives, although they may be suitable for double salt formation, would appear to be prohibitive of practical application. The metals employed in my invention are of the coordinating type, probably exerting, as previously stated, auxiliary valencies in their complex ion forming compounds.

Some similar compounds have been heretofore described containing ammonia, pyridine, ethylene

diamine, etc., but none have been described containing nicotine. Most of my compounds have no corresponding analogs in any other organic base complex salts now known in the art. In the following description when a metal salt or metal is referred to generally, it is to be understood that one of the metals or salts designated above is indicated.

Other metals such as titanium, platinum, gold, etc., would serve to produce many if not all of the corresponding nicotine complex salts but their costs would be too high for use as insecticides and fungicides generally. The process involved in the preparation of my new compounds is closely related to their usual composition as represented by the formula $MX_n \cdot n(C_{10}H_{14}N_2 \cdot HX)$ where M represents one atom of a metal of the group copper, zinc, nickel, cobalt, cadmium and iron. X represents a univalent radical such as a hydrocyanic, thiocyanic, picric, benzoic, salicylic, or o-benzoyl benzoic acid radical. The valency of the metal M is thus represented by n and is 2 with all metals except iron and cobalt where it may be either 2 or 3. It is evident that the ferrous salts may tend to oxidize in the air and can be prepared only by the exclusion of oxygen such as the double nicotine ferrous ferrocyanide. The ferrous nicotine double thiocyanate, however, is a crystalline compound easily prepared before appreciable oxidation results.

With polyvalent acids such as hydroferrocyanic with a valency of 4, n is 4, and the formula for a bivalent metal would be

$$M_2(FeCy_6) \cdot 4C_{10}H_{14}N_2 \cdot H_4FeCy_6$$

For the purpose of preparation, one half of the acid is used to form the metallic salt and the other half to form the equivalent nicotine salt. The percentage of nicotine may not always correspond to the general formula

$$MX_n \cdot n(C_{10}H_{14}N_2 \cdot HX)$$

although approximated closely with the benzoates, picrates and salicylates. The highly complex nature of the double cyanides, ferrocyanides, and ferricyanides prevents an exact formulation of the resulting compound.

In the preparation of new compounds it should be understood that the individual solutions and the final resulting mixture containing the precipitated double salt should be adjusted to keep within the range of pH 5–7.5. If the normal salt is desired in the greatest yield it is best to have all solutions slightly acid, around pH 5, and to make the final adjustment to pH 7–7.5 to complete the precipitation. Excessive acidity will tend to dissolve and disrupt the compounds while excessive alkalinity will form admixed basic salts with a lowered content of nicotine. The resulting compounds of this invention represent essentially combinations of neutral salts. The ferrocyanide compounds are very insoluble, and colloidal in nature causing difficulty in filtration. They may be found particularly adaptable to spray mixtures.

In order to spread the action of the dry powders it may be desirable to dilute them with such materials as talc, starch, kaolin and other neutral products commonly used as diluents for insecticides.

In the preparation of the copper, nickel and cobalt compounds I prefer to avoid the presence of ammonium salts which tend to prevent complete precipitation, but with the zinc cadmium and iron salts they do not interfere; but may actually assist the crystallization of the zinc and cadmium double salts by preventing the formation of basic salts of these metals.

The double salts containing ferrocyanide and ferricyanide are probably super complex salts wherein the nicotine salts are conjugated with the metallic ferro and ferricyanides. There are two general processes employed in the preparation of my compounds both of which are based on the formula $MX_n \cdot n(C_{10}H_{14}N_2 \cdot HX)$. Process No. 1, hereinafter described, can be employed with many but not all of them. It may be employed when the metallic salt can be first readily prepared and then brought into contact with the equivalent nicotine salt. For example, copper benzoate can be first prepared and washed free of soluble salts and brought into contact with the nicotine benzoate dissolved in water. Copper salicylate, however, is very soluble and process No. 2 should be employed. These two processes are as follows:

Process No. 1.—In water solution one molecule of the metallic salt of the metal combined with the acid selected is treated with the equivalent amount of the nicotine salt of the acid. After varying intervals of time the maximum of the nicotine salt is removed from the solution. The freshly prepared metallic salt while still wet reacts more rapidly than after drying. If the nicotine salt of the acid is not available, equivalent proportions may be used of a soluble salt of nicotine with a soluble salt of the acid where the metal may be sodium, potassium, ammonium, calcium, magnesium or other non-coordinating metal.

Process No. 2.—This process is generally applicable to all compounds and consists in bringing together a soluble salt of the metal with the equivalent quantity of a soluble salt of the acid such as the sodium, potassium, ammonium, calcium magnesium or other non-coordinating metal salt and the equivalent quantity of the nicotine salt of the acid. If the nicotine salt is not available it is only necessary to use an equivalent amount of some nicotine salt with an equivalent of the soluble salt of the acid such as the sodium, potassium, ammonium, calcium, magnesium or other non-coordinating metal. The double salt obtained will contain only the acid selected from the group of polymerizing acids of this invention and, if desired, may be washed free of contaminating soluble salts.

The following examples illustrate in more detail the manner of preparing the new compounds of my invention.

Example 1

One mol of copper acetate is added to a mixture of 2 mols of sodium benzoate and 2 mols of nicotine benzoate all in water solution. If normal solutions of these three compounds are used the precipitated copper nicotine compound forms a rather dense mixture. I prefer, therefore, dilution with more water before filtration is made. A slight excess of dissolved benzoic acid will produce a mixture between pH 5 and pH 7. The pH may be adjusted to 7–7.5 with dilute nicotine alkaloid solution in water to secure maximum precipitation yet avoid the production of basic (C. R. S.) salts. The washed and dried copper nicotine benzoate analyzes 7.7% for copper and 37% to 38% for nicotine; theory for Cu is 7.27% and for nicotine 37.1%.

Example 2

One mol of copper sulphate is added to a mixture of 2 mols of sodium thiocyanate and 2 mols of an equivalent nicotine thiocyanate produced by a mixture of 2 mols of nicotine hydrochloride and 2 mols of sodium thiocyanate. Cupric nicotine thiocyanate is produced as a bright green colored product quite insoluble in water. On boiling with alkalies, cupric oxide is formed.

Example 3

Copper acetate in aqueous solution is added to a mixture of 2 mols of sodium cyanide and 1 mol of a neutral nicotine salt until a slight excess of copper is present. The salt to be expected, corresponding to the formula expected

$$Cu(CN)_2 \cdot 2C_{10}H_{14}N_2HCN$$

loses cyanogen, and a brown insoluble salt analyzing as nicotine cuprous cyanide is produced.

Example 4

Two mols of copper acetate is added to a mixture of 2 mols of a ferrocyanide salt and 4 mols of nicotine hydrochloride. The double ferrocyanide has a bluish red color, filters well, although the gelatinous product dries slowly.

Example 5

Two mols of zinc acetate may be used instead of the copper acetate in Example 4. The resulting product is yellowish white, highly colloidal, and filters slowly.

Example 6

Instead of copper sulphate in Example 2, nickel acetate may be used to obtain a crystalline blue double thiocyanate.

Example 7

Instead of copper sulphate in Example 2, cobalt acetate may be used to obtain a crystalline pink double salt.

Example 8

Instead of copper sulphate in Example 2, cadmium acetate may be used to obtain a crystalline white double salt.

Example 9

One mol of ferric chloride and a mixture of 6 mols of sodium thiocyanate and 3 mols of nicotine monohydrochloride results in a double salt that is bluish red to red in color but turns brownish on prolonged washing, probably due to hydrolysis.

Example 10

One mol of ferrous ammonium sulphate dissolved in water and added to a mixture of 4 mols of sodium thiocyanate and 2 mols of nicotine monohydrochloride results in the precipitation of a double salt that is a brownish white crystalline product.

Example 11

To a mixture of two mols of potassium ferrocyanide and 4 mols of nicotine hydrochloride a solution of ferric ammonium sulphate is added containing one molecular equivalent of Fe'''. The resulting blue double salt is quite insoluble and filters with some difficulty, leaving a gelatinous product.

Example 12

If instead of copper acetate in Example 4 nickel acetate is used, a greenish blue double salt of nickel nicotine ferrocyanide is produced.

Example 13

Using 1 mol of zinc chloride and 4 mols of potassium cyanide and 2 mols of nicotine hydrochloride, a white crystalline double salt of zinc nicotine cyanide is obtained. The use of some ammonium chloride seems to help the formation of fine crystals which are easier to filter.

In the examples given above the acetates of the metals have usually been employed as leading to purer products. In commercial practice it is advisable to use the sulphates of the metals and calcium salts of the acids whenever possible, since the resulting calcium sulphate

$$(CaSO_4 \cdot 2H_2O)$$

is nonhygroscopic and need not be washed out of the material when the resulting nicotine double salt is to be employed as an insecticide in dust form.

Having thus described my invention, I claim:

1. An insecticidal and fungicidal agent comprising a nicotine complex salt of the formula $MX_n \cdot n(C_{10}H_{14}N_2 \cdot HX)$ in which M is a polyvalent coordinating metal taken from the group consisting of copper, zinc, nickel, cadmium, iron, and cobalt; n is 2 or 3; and X is a radical of the group consisting of —CN and —CNS, both X's being identical; n being the valence of the metal M.

2. The agent of claim 1 in which the acid radical is —CN.

3. The agent of claim 1 in which the acid radical is —CNS.

4. An insecticidal and fungicidal agent comprising the cupric nicotine thiocyanate of the formula $Cu(CNS)_2 \cdot 2(C_{10}H_{14}N_2 \cdot HCNS)$.

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