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REACTION PRODUCTS OF ESTERS OF POLYPHOSPHORIC ACIDS AND HEAVY METAL OXIDES AND METHOD OF MAKING SAME

Robert Harry Hurt, Charlottesville, Va., assignor to Virginia Polytechnic Institute, Blacksburg, Va.

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24 Claims. (Cl. 260—430)

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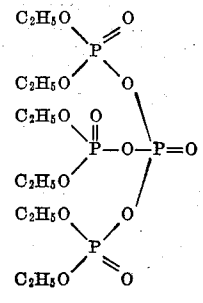
The present invention relates generally to certain novel compositions of matter possessing both insecticidal and fungicidal properties and to the methods of producing such compositions.

More particularly, this invention relates to certain novel chemical methods adapted to be employed in the mercuration or silveration of the alkyl esters of polyphosphoric acid and to the combination insecticidal-fungicidal products resulting therefrom.

As is well-known to those skilled in the art, two of the principal problems facing growers of apples and citrus fruits involve the control of various types of fungous diseases and of certain insect pests which attack these crops. In the past, these problems have ordinarily been met by the separate application of various known insecticides and fungicides, thereby necessitating a duplication of labor and a resultant increase in costs to the grower.

From another standpoint, it is well recognized that the application of certain of the chemical materials employed in the control of insect pests and fungous diseases may, in some cases, involve a certain element of hazard to the workmen, in view of the relatively toxic nature of the materials employed. This has been particularly true in the case of certain mercury compounds which are generally rather difficult to handle and frequently produce toxic symptoms among workers handling these materials.

The insecticide art has advanced rather rapidly in recent years, although much still remains to be learned concerning the chemistry and toxic properties of certain of the complex organic compounds which were developed in this country and particularly in Germany just prior to and during World War II. For example, in the text book of Dr. E. H. Frear, entitled "Chemistry of Insecticides, Fungicides and Herbicides," and published by D. Van Nostrand Company, Inc. in 1948 (2nd edition), the author refers, at page 100, to an insecticide known as hexaethyl tetraphosphate. The discovery of this material is attributed to a German, G. Schrader, and Dr. Frear has set forth certain of the known properties of this material as well as the following tentative structural formula:



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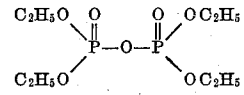
For a further disclosure of the hexaesters of tetraphosphoric acid, reference is made to the U. S. patent issued December 7, 1943, to Gerhard Schrader, No. 2,336,302. This patent embodies a disclosure of a method of making such products and specifically describes the manufacture of the tetraphosphoric acid hexaethyl ester.

Another insecticidal compound of particular interest in connection with the present disclosure is the material known as tetraethyl pyrophosphate. A discussion of the properties of this material is also set forth in Dr. Frear's book (supra) at pages 101 and 102, and a tentative structural formula of this compound is set forth as follows:



As indicated above, it is quite generally known that the alkyl esters of the polyphosphoric acids, particularly those referred to as hexaethyl tetraphosphate and tetraethyl pyrophosphate, possess effective insecticidal properties and are especially useful for the control of soft-bodied insects such as aphis and mites. A method of producing neutral esters of molecularly dehydrated phosphoric acids is set forth in U. S. Patent No. 2,402,703, issued June 25, 1946, to Willard H. Woodstock. However, it is also known that these compositions possess substantially no fungicidal properties, and in addition, tend to hydrolyze and thus lose their insecticidal value within a short time after application as a spray to growing crops.

It is also common knowledge in the art that many of the salts of certain of the heavy metals possess fungicidal properties, although unfortunately, many of these organic and inorganic compounds are also toxic to all other forms of life. For example, a discussion of such organic and inorganic mercury compounds is set forth in Dr. Frear's book (supra) at pages 250 to 254, wherein specific reference is made to mercuric chloride (corrosive sublimate—$HgCl_2$), mercurous chloride (calomel—HgCl or $HgCl_2$), mercuric oxide (yellow oxide of mercury—HgO), ethyl mercuric chloride (C_2H_5HgCl), ethyl mercuric iodide (C_2H_5HgI), ethyl mercuric phosphate, and a rather large number of phenyl mercuric salts or other phenyl mercury derivatives.

The fungicidal properties of certain alkyl and aryl mercury hydrocarbons, as well as methods of producing the same, are also discussed in U. S. Patent No. 1,770,887, issued to Morris S. Kharasch on July 15, 1930, and in the patent to Lee C. Holt, No. 2,344,872, issued March 21, 1944.

In the light of the foregoing, the principal object of the present invention is to produce certain novel compositions of matter having both insecticidal and fungicidal properties.

Another object of the invention is to provide certain novel methods of producing the combined insecticidal and fungicidal materials of the type described.

A further object of the invention is to provide effective fungicidal and insecticidal materials adapted for application to growing crops by means of a single operation.

The foregoing, as well as other and further objects and advantages of the present invention will become more readily apparent to one skilled in the art from a consideration of the following detailed specification, together with the specific examples set forth therein and the claims appended thereto.

The present invention is based largely upon the discovery that certain of the alkyl esters of polyphosphoric acid may be reacted with an oxide of a heavy metal such as yellow mercuric oxide or silver oxide to produce new chemical compounds possessing both fungicidal and insecticidal properties. In what is perhaps its broadest aspect, therefore, this invention comprises the mercuration or silveration of an alkyl ester of polyphosphoric acid and the reaction products thereof.

As a subsidiary result, it has also been observed that the mercurated ester compositions resulting from the reaction of the polyphosphoric acid esters with yellow oxide of mercury are considerably more stable than are the esters alone. Furthermore, while the alkyl esters of polyphosphoric acids are known to possess insecticidal properties, it has been observed that an addition of the mercuric oxide to the molecular structure of the esters, in addition to producing the fungicidal properties referred to, also has the effect of increasing the insecticidal properties of the compounds, particularly against sucking insects such as aphis, mites and other soft-bodied insects commonly found on apple and citrus foliage.

Referring now to the preferred methods of producing the compounds referred to above, I have discovered that the mercuration or silveration of the alkyl esters of polyphosphoric acid may be accomplished by two different methods, as follows:

METHOD NO. 1

In accordance with this method, the alkyl ester of polyphosphoric acid is first prepared or synthesized in any convenient and well-known manner and this product is then reacted with yellow mercuric oxide in substantially molar proportions to produce the mercurated alkyl ester of polyphosphoric acid. In a similar manner, the alkyl esters of polyphosphoric acid may be reacted with silver oxide to produce the silver alkyl esters of polyphosphoric acid. Furthermore, a mixture of yellow oxide of mercury and silver oxide may be reacted with the alkyl ester of polyphosphoric acid to produce a composition of matter which contains both mercury and silver in the molecular structure. Where both mercuric oxide and silver oxide are employed, any desirable proportions of these ingredients may be used, although I prefer to use equal portions of each.

In preparing these new compounds, the reactants, as indicated above, are preferably provided in substantially molar proportions. However, the criterion in each case is to choose proportions of the ester and mercury such that the resultant

product will have the proper percentage of each when it is made into final spray form for application to the crops. The maximum amount of metallic mercury in the final spray form should not exceed 1 part in 5,000, and preferably ranges from 1 part in 10,000 to 1 part in 20,000, or a preferred equivalent of approximately 20 grams per 100 gallons of spray solution. These figures, of course, pertain to the mercury in combination in the compound which preferably contains from 5 per cent to 10 per cent metallic mercury in combination, and it will be understood that preferably there is no free mercury as such in the compound. The proportion of the ester will likewise depend upon the quantity required in the final spray solution, and in accordance with the preferred practice, this value is selected so as to provide from one-half pint to one pint of ester for each 100 gallons of the spray.

As indicated above, black silver oxide may be used in approximately the same proportions as yellow mercuric oxide, although I prefer to employ a proportion of each in the reaction. I have observed that the mercury appears to catalyze the reaction, thereby both speeding it up and also making it possible to combine a larger proportion of silver with the ester. Since the metallic silver has less fungicidal value than mercury, this is, of course, a desirable side effect when it is desired to employ silver for its fungicidal action.

It may also be noted that the red oxide of mercury is operable in the reaction in place of yellow mercuric oxide. Also, it is preferable to add a trace of chromium trioxide (CrO_3) in order to stabilize the compound against the possible precipitation of mercury caused by a reaction with soluble chlorides in ordinary city water which may be used in making up the spray solution.

In accordance with Method No. 1, the polyethyl esters of orthophosphoric acid or the tetraethyl esters of pyrophosphoric acid may be reacted with yellow oxide of mercury in a suitable open reaction chamber. The reaction chamber is preferably made of iron or steel and should be provided with suitable apparatus to produce agitation in order to keep the mercury oxide in suspension until the reaction is completed. The application of heat is employed to start the reaction which commences at around 70° C. It is not necessary to provide reflux apparatus. Once the reaction has started, it is exothermic and although cooling need not be resorted to, the application of heat may be discontinued as soon as the reaction is well under way.

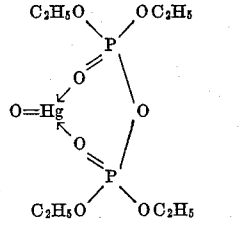
As indicated above, the yellow oxide of mercury may be reacted with varying amounts of the alkyl esters up to the point of chemical saturation. Furthermore, although the proportions of the reactants employed are based generally upon the amount of the finished product desired for use as a spray composition when mixed with 100 gallons of water, such proportions may also be based upon the solvent action of the alkyl esters upon the mercurated alkyl esters constituting the end products.

Although I am not sure as to the exact chemical reaction which takes place, it is believed that the mercuric oxide forms a salt-like combination with the alkyl esters, probably reacting at the double bonds between the phosphorus and oxygen atoms. Typical equations, and a possible structural formula for a finished product in accordance with Equation 2 are set forth below, in

which R in each case designates a chain hydrocarbon or alkyl radical.

(1) $R_6P_4O_{13} + 2HgO \longrightarrow R_6P_4Hg_2O_{15}$

(2) $R_4P_2O_7 + HgO \longrightarrow R_4P_2HgO_8$



Typical examples of the improved method set forth above as Method No. 1, are as follows:

Example A

Mercurated polyethyl tetraphosphate may be prepared as follows: Into a suitable reaction chamber of the type described above, place 500 grams of hexaethyl tetraphosphate. Into the ester, approximately 60 grams of yellow oxide of mercury are slowly added while the mixture is being thoroughly agitated within the reaction vessel. As the mixing takes place, heat is gradually applied to the container with continuous agitation of the contents until the temperature of the reactants has reached approximately 70° C. At this temperature, the reaction commences and, due to its exothermic nature, sufficient heat is usually produced to complete the chemical reaction, so that no further heat need be applied externally. The resultant chemical composition upon cooling is a dark syrup-like liquid having a specific gravity ranging from approximately 1.30 to 1.5.

Example B

Mercurated tetraethyl pyrophosphate is made as follows: Place approximately 490 grams of tetraethyl pyrophosphate in an open iron reaction chamber of the type described above. To this ester, slowly add approximately 60 grams of yellow oxide of mercury while thoroughly agitating the mixture. Heat may then be applied gradually to the container with continued constant agitation of the contents until the temperature of the reactants has reached approximately 80° C. Although this reaction is also exothermic, the heat produced thereby is usually not sufficient to complete the reaction and, therefore, the application of heat is continued in sufficient amount to maintain the temperature of the reactants at approximately 80° C. The end product of this reaction is a dark syrup-like liquid having a specific gravity which ranges from approximately 1.25 to 1.35.

By following the procedure hereinabove outlined for producing the reaction according to Method No. 1 and as set forth in Example A, it is possible to combine the following reagents in approximately the proportions given:

Example C

Approximately 480 grams of tetramethyl pyrophosphate may be reacted with approximately 36 grams of yellow oxide of mercury.

It is also possible to react certain of the higher alkyl esters of polyphosphoric acid, and I have, for example, successfully reacted molar proportions of yellow mercuric oxide and the polybutyl ester of orthophosphoric acid. However, esters having alkyl radicals of 4 chain carbons (butyl or higher) are insoluble in the usual solvents employed in making insecticide-fungicide sprays. For this reason, the butyl and higher esters of polyphosphoric acid are of relatively less importance as compared, for example, with the mercurated hexaethyl tetraphosphate or mercurated tetraethyl pyrophosphate, although these esters, such as hexabutyl tetraphosphate, may be mixed with inert powdered ingredients to form an insecticide-fungicide dust, if desired.

METHOD NO. 2

The mercurated alkyl esters previously described may also be made in accordance with a second method wherein the desired trialkyl phosphate is brought together with substantially molar proportions of yellow oxide of mercury and phosphoric anhydride within a suitable reaction chamber. In this method of procedure, the trialkyl phosphate is continuously agitated and heated as the yellow oxide of mercury is added, and when the latter has been thoroughly mixed with the phosphate, the proper amount of phosphoric anhydride is then slowly added while the mixture is vigorously agitated. Heating of the mixture of the three ingredients is then continued until the reaction is completed, at which time substantially no yellow oxide of mercury or phosphoric anhydride will remain uncombined. Should the reaction product be cloudy, indicating the presence of residual uncombined phosphoric anhydride, the addition of a trace of chromium trioxide will serve to hasten the reaction to completion.

A typical example of the production of mercurated alkyl ester of polyphosphoric acid produced in accordance with Method No. 2 may be set forth as follows:

Example D

Into a suitable reaction chamber of the type described above, place approximately 360 grams of triethyl phosphate. With continuous agitation of the triethyl phosphate, slowly add to this mixture approximately 60 grams of yellow oxide of mercury. Continue the vigorous agitation of the mixture of triethyl phosphate and mercuric oxide while adding approximately 140 grams of phosphoric anhydride to the mixture. Agitation should be continued until substantially all of the yellow oxide of mercury and phosphoric anhydride have completely combined with the triethyl phosphate, and although the reaction is exothermic, external heat may be applied if necessary, so long as the temperature of the reactants does not exceed 100° C. The chemical product resulting from this reaction is a dark syrup-like liquid with a specific gravity ranging from approximately 1.3 to 1.5.

Although the available experimental data presently available is insufficient to form a basis for any definite conclusion, limited tests on live mice clearly indicate that the mercurated esters of polyphosphoric acid are somewhat less poisonous to warm-blooded animals than are the unmercurated esters such as tetraethyl pyrophosphate or hexaethyl teteraphosphate. This is a matter of considerable importance to growers, since there is always some danger inherent in the use of insecticides and fungicides, and where my improved compound has been used, workmen spraying for as long as three days at the recommended dilution have not been observed to have any toxic reaction whatsoever.

As indicated above, the preferred method of application of the mercurated esters of polyphos-

phoric acid is in the form of a liquid spray using approximately one-half pint of the mercurated ester for each 100 gallons of spray solution. In making up the spray solution, the order of addition is relatively unimportant, although I prefer to add the mercurated ester to the desired volume of water.

It may also be noted that while it is possible to react a sufficient quantity of mercuric oxide with the ester to incorporate as much as 40 per cent metallic mercury in the concentrated resultant product, there does not appear to be any practical utility for solutions of this strength. As a matter of fact, the higher concentrations of mercury are generally undersirable, due to their greater toxicity, and since only around 5 to 6 per cent of metallic mercury is required to secure satisfactory fungicidal properties, the higher concentrates are not generally employed. I have observed, however, that the mercury in combination in the ester definitely slows down the hydrolysis of the resultant product. Thus, the mercurated alkyl esters of polyphosphoric acid tend to retain their insecticidal and fungicidal properties for a relatively long period after application as a liquid spray.

Obviously, numerous other modifications, alterations and deviations from the specific materials and process steps disclosed herein solely for the purpose of illustration will occur to those skilled in the art, without departing from the spirit or scope of the invention as set forth in the appended claims.

Having thus described my invention, what I claim as novel and desire to secure by Letters Patent of the United States is:

1. The heavy metal polyalkyl reaction product of an ester of polyphosphoric acid and an oxide of a heavy metal.

2. The heavy metal polyalkyl reaction product of an alkyl ester of polyphosphoric acid and mercuric oxide.

3. The heavy metal polyalkyl reaction product of an alkyl ester of polyphosphoric acid and silver oxide.

4. The heavy metal polyalkyl reaction product of an alkyl ester of polyphosphoric acid and a mixture of mercuric oxide and silver oxide.

5. The mercurated polyalkyl reaction product of hexaethyl tetraphosphate and yellow mercuric oxide.

6. The mercurated polyalkyl reaction product of tetraethyl pyrophosphate and yellow mercuric oxide.

7. The mercurated polyalkyl reaction product of tetramethyl pyrophosphate and yellow mercuric oxide.

8. The mercurated polyalkyl reaction product of a polybutyl ester of orthophosphoric acid and yellow mercuric oxide.

9. The mercurated polyalkyl reaction product of triethyl phosphate, yellow mercuric oxide, and phosphoric anhydride.

10. The method of preparing a chemical compound characterized by marked insecticidal and fungicidal properties which comprises reacting

a polyalkyl ester of polyphosphoric acid with an oxide of a heavy metal.

11. The method of preparing an insecticidal-fungicidal composition which comprises reacting a polyalkyl ester of polyphosphoric acid with mercuric oxide.

12. The method of preparing an insecticidal-fungicidal composition which comprises reacting a polyalkyl ester of polyphosphoric acid with silver oxide.

13. The method of preparing an insecticidal-fungicidal composition which comprises reacting a polyalkyl ester of polyphosphoric acid with a mixture of mercuric oxide and silver oxide.

14. The method of preparing an insecticidal-fungicidal composition which comprises reacting hexaethyl tetraphosphate with yellow mercuric oxide.

15. The method of preparing an insecticidal-fungicidal composition which comprises reacting tetraethyl pyrophosphate with yellow mercuric oxide.

16. The method of preparing an insecticidal-fungicidal composition which comprises reacting tetramethyl pyrophosphate with yellow mercuric oxide.

17. The method of preparing an insecticidal-fungicidal composition which comprises reacting a polybutyl ester of orthophosphoric acid with yellow mercuric oxide.

18. The method of preparing a mercurated polyalkyl ester of orthophosphoric acid having insecticidal and fungicidal properties which comprises reacting triethyl phosphate, yellow mercuric oxide, and phosphoric anhydride.

19. The method of preparing an insecticidal-fungicidal composition which comprises reacting an ester of polyphosphoric acid, an oxide of a heavy metal, and chromium trioxide.

20. The method of preparing a mercurated polyalkyl ester of orthophosphoric acid having insecticidal and fungicidal properties which comprises reacting triethyl phosphate, yellow mercuric oxide, phosphoric anhydride, and chromium trioxide.

21. The mercurated alkyl ester resulting from the reaction of an alkyl ester of polyphosphoric acid, mercuric oxide, and chromium trioxide.

22. The silverated alkyl ester produced by reaction of an alkyl ester of polyphosphoric acid, silver oxide, and chromium trioxide.

23. The heavy metal alkyl ester produced by reaction of an alkyl ester of polyphosphoric acid, mercuric oxide, silver oxide, and chromium trioxide.

24. The mercurated alkyl ester produced by the reaction of hexaethyl tetraphosphate, mercuric oxide, and chromium trioxide.

ROBERT HARRY HURT.

REFERENCES CITED

The following references are of record in the file of this patent:

C. A., vol. 26, page 5932.

Arbusow et al.: J. Prakt. Chem., vol. 130, 1931.