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UREA ADDUCTS OF QUATERNARY
AMMONIUM COMPOUNDS

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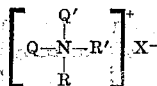
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1

This invention relates to quaternary ammonium compounds. More specifically, it relates to a novel series of chemical compounds composed essentially of a quaternary ammonium compound and urea.

Quaternary ammonium compounds are well-known compositions of matter, ionic in nature, having the following structural formula:



where the substituents on the nitrogen atom represent the same or different organic radicals, and X represents an anion. These materials are known to be useful in various fields, depending upon the specific substituents contained therein. They have been used, for example, as germicides, fungicides, surface-active agents, therapeutic agents, and the like. Their utilization has been handicapped, however, owing to the fact that they are highly hygroscopic materials, and are therefore obtained as sticky or pasty semi-solid masses, which are difficult to measure, handle, and store.

We have now discovered that quaternary ammonium compounds of a certain class can be converted into free-flowing, talc-like powders by reaction with urea according to methods well-known in the art, to form crystalline urea adducts thereof. The said class of quaternary ammonium compounds is limited as follows with respect to the substituents on the nitrogen atom: (1) there must be at least one straight-chain organic radical containing at least five methylene groups; and (2) there should not be more than one cyclic radical, and said cyclic radical should be carboxylic, should contain not more than six carbon atoms in the ring, and should be attached to the nitrogen atom through an aliphatic linkage. The resulting products have outstanding advantages in many uses. They are non-hygroscopic, free-flowing, talc-like powders which are easily packaged, measured, blended, and dissolved. They retain their free-flowing, powdery character in storage and under conditions of high humidity. They are readily produced in constant and unvarying composition, and can therefore be standardized on a potency basis. They may be readily combined with other ingredients in dusting powders, in aqueous solutions, or in emulsions. The urea, being non-ionic, does not interfere with the characteristic activity of the quaternary ammonium salt (for example, surface activity, or fungicidal or germicidal character).

2

The surface activity of the quaternary ammonium compound reduces the surface tension of aqueous solutions of the adduct, and facilitates spreading and penetration of the urea in certain applications. All of these advantages represent striking improvements over the quaternary ammonium compounds of the prior art.

One object of our invention is to convert quaternary ammonium compounds into a form more readily and conveniently stored, handled, measured, and applied. Another object is to convert urea into a more effectively utilizable form. Another object is to prepare a chemical combination of urea and a quaternary ammonium compound having synergistic properties as a nutrient and an antibiotic when employed in plant sprays. A further object is to separate quaternary ammonium compounds into classes according to structural configuration. Other objects of our invention will be apparent from the description thereof and the appended claims.

The preparation of our new compositions of matter is carried out by reacting urea with a quaternary ammonium compound of our defined class according to methods described in the prior art. The quaternary ammonium compound is preferably dissolved in an organic liquid, which serves as a diluent to produce a solution of low viscosity, and the resulting solution is contacted with urea and a urea solvent at a temperature between about 0 and 60° C., preferably between about 20 and 40° C., until the reaction is complete, ordinarily between about 0.1 and 2 hours. The resulting reaction product is a slurry of the desired urea adduct in the diluent liquid. The slurry is subjected to filtration, settling and decantation, centrifugation, or the like, to separate the adduct, and the adduct is washed with a quantity of cold diluent liquid to remove entrained mother liquor therefrom. The washed solid is then dried. The dry solid is the new composition of our invention, suitable without further treatment for the many uses to which it is adapted.

Suitable diluents for the quaternary ammonium compounds include methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, ethylene glycol, and the like. These solvents function simultaneously to dissolve the quaternary ammonium compounds and reduce the viscosity thereof, and to activate the urea for adduct formation.

For complete reaction of the quaternary ammonium compound with urea, the ratio of urea to quaternary ammonium compound should be

at least one mole of urea per methylene group in the straight-chain organic radicals containing more than 5 methylene groups which are attached to the nitrogen atom. When substantially pure adducts are desired, uncontaminated with free urea, a smaller ratio of urea should be employed.

It will be apparent that numerous variations of the above procedure may be employed for making our new compositions. The following variations are illustrative:

1. The quaternary ammonium compound in excess is stirred at room temperature with a saturated solution of urea in a urea solvent, such as a lower aliphatic (C₁ to C₆) alcohol. The adduct that precipitates is filtered off, washed with a low-boiling solvent such as acetone or ether, and dried. The unreacted quaternary ammonium compound in the wash liquor is recycled.

2. Theoretical proportions of urea and the quaternary ammonium compound are dissolved in a lower aliphatic alcohol, and the solution is spray-dried.

3. A concentrated solution (for example, 50 to 75 percent by weight) of the quaternary ammonium compound in a lower aliphatic alcohol is mixed with the theoretical proportion of dry powdered urea, the mixture is stirred until it becomes homogeneous, and the resulting slurry is dried.

4. An unsaturated alcoholic solution of urea and a quaternary ammonium compound in approximately theoretical proportions is diluted with an organic liquid which functions as an alcohol solvent and a urea-adduct antisolvent. The precipitated adduct is filtered off and dried.

5. A mixture of quaternary ammonium compounds is treated with urea according to any of the foregoing methods. The resulting urea adduct contains only our defined class of urea-reactive quaternary ammonium compounds. These procedures therefore afford a method for separating the said class of quaternary ammonium compounds from other types.

Our invention will be more fully understood from the following specific examples:

Example I

Ten grams of a 75 percent by weight solution of dimethyldilaurylammonium bromide in isopropyl alcohol was mixed with a saturated solution of urea in methanol containing ten grams of urea, and the mixture was agitated approximately 15 minutes at room temperature. The reaction mixture was then diluted with 50 milliliters of diethyl ether and was filtered. The solids were washed with an additional quantity of diethyl ether and were dried in air. The resulting product was a fine white powder containing 5.25 percent by weight of bromine. This corresponds to a ratio of one mole of the quaternary ammonium salt to 17.6 moles of urea, or 33 percent by weight of quaternary ammonium salt in the urea adduct. Fungicidal tests on the adduct revealed that its fungicidal potency against *Sclerotinia fructicola* was exactly proportional to the content of quaternary ammonium salt, the MLD-50 being obtained at a concentration of 2.8 milligrams of quaternary ammonium salt per liter, and MLD-95 at 5.9 milligrams per liter.

Example II

Twenty grams of a 50 percent by weight solution of benzyltrimethylaurylammonium chloride in isopropyl alcohol was treated as described in

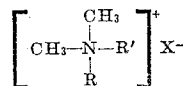
Example I with ten grams of urea in methanol. The resulting white powder analyzed 4.15 percent by weight chlorine, corresponding to one mole of ammonium salt per 8.6 moles of urea, or 40 percent by weight quaternary ammonium salt in the adduct. Consistent with this ratio, the fungicidal MLD-50 against *Sclerotinia fructicola* was obtained at a concentration of 1.7 milligrams of quaternary ammonium salt per liter, and the MLD-95 at 2.4 milligrams per liter.

Example III

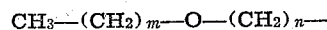
Urea adducts were similarly prepared from the following quaternary ammonium compounds:

- Benzyltrimethylauryloxymethylammonium chloride.
- Benzyltrimethylaurylthiomethylammonium chloride.
- Lauryltrimethylammonium chloride.

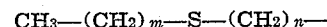
The quaternary ammonium compounds from which our novel compositions are derived are substituted dimethylammonium compounds having the following structural formula,



where R and R' comprise at least one straight-chain organic radical containing at least five methylene groups, where R and R' together contain not more than one carbocyclic-substituted aliphatic radical, said carbocyclic-substituted aliphatic radical containing not more than six carbon atoms in the ring, and where X represents an anion, such as halogen, sulfate, hydroxyl, or n-acyloxy group. The said straight-chain group may be n-alkyl, n-alkenyl, n-alkynyl, n-alkadienyl, n-oxaalkyl



n-polyoxaalkyl, n-thiaalkyl



n-polythiaalkyl, and the like, where m and n represent zero or positive integers which must total at least five, and where X represents halogen. The urea-reactivity of the straight-chain organic radical is not affected by the substitution thereon of hydroxyl or fluorine in any position, or by substitution thereon of other halogen, amino, or mercapto in the omega position. The carbocyclic group may be cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexenyl, phenyl, and the like, and may contain a halogen, hydroxyl, or mercapto substituent in the para position. The most useful group of our new compositions which we have so far prepared are obtained from quaternary ammonium salts containing one or two C₁₀-C₂₀ n-alkyl groups. These compounds have excellent germicidal, fungicidal, and surface-active properties, which are retained and improved when the compounds are reacted with urea.

Our new compositions are useful in a wide range of applications. They may be used as a combination plant food and fungicide for fruit trees and plants in general. For this purpose, they can be conveniently used as a dust, owing to the fact that they are free-flowing, non-hygroscopic powders; and they can conveniently be combined with insecticidal agents and inert materials which are commonly applied separately. Since garden crops or ornamental plants are commonly dusted in the morning when the plants are wet with dew, the use of our new compositions or materials comprised thereof at such times is distinctly advantageous, permitting rapid decomposition of the urea adduct and immediate feed-

ing and fungicidal action by the urea and the quaternary ammonium salt. Alternatively, our new compositions can be used advantageously as a component of sprays for plants and trees. In this connection, the surface-active characteristics of the quaternary ammonium compounds are highly advantageous. When the adduct is added to water, it decomposes, yielding a solution which has a lower surface tension than a comparable urea solution and for this reason being more capable and efficient in feeding nitrogen to plants. If a higher ratio of urea is desired, an additional quantity of urea can be blended with the adduct, owing to the powdery form of the latter. Our new compositions are also useful in pharmaceutical preparations, for example in mouth washes, tooth pastes, and the like. They are especially useful in tooth powders, where their non-hygroscopic nature is essential, and where their combined germicidal and ammonia-producing actions are highly desirable. Many other uses will be apparent to those skilled in the art.

While we have described our invention in connection with certain specific embodiments thereof, it is to be understood that we are not limited thereto. The compositions of our invention are new and useful broadly within the scope of the disclosure thereof, and it is further to be understood that any modifications or equivalents that would ordinarily occur to one skilled in the art are to be considered as lying within the scope of our invention.

In accordance with the foregoing description, we claim as our invention:

1. An adduct of urea and a quaternary dimethylammonium compound having as substituents on the nitrogen atom thereof (1) at least one straight-chain organic radical containing at least five methylene groups and (2) an aliphatic radical containing not more than one carbocyclic-substituent, said carbocyclic substituent containing not more than six carbon atoms in the ring, said quaternary dimethylammonium compound being otherwise free from functional groups reactive with urea.

2. The composition of claim 1 wherein said quaternary dimethylammonium compound has as substituents on the nitrogen atom thereof at least one $C_{10}=C_{20}$ n-alkyl radical.

3. The composition of claim 1 wherein said quaternary dimethylammonium compound has as substituents on the nitrogen atom thereof at least one n-oxaalkyl radical containing at least five methylene groups.

4. The composition of claim 1 wherein said quaternary dimethylammonium compound has as substituents on the nitrogen atom thereof at least one n-thiaalkyl radical containing at least five methylene groups.

5. An adduct of urea and a quaternary dimethylammonium compound having as substituents on the nitrogen atom thereof (1) at least

one straight-chain organic radical containing at least five methylene groups and (2) an aliphatic radical free from cyclic substituents, said quaternary dimethylammonium compound being otherwise free from functional groups reactive with urea.

6. An adduct of urea and a dialkyldimethylammonium compound wherein at least one of said alkyl radicals is an n-alkyl radical containing at least six carbon atoms.

7. An adduct of urea and a dialkyldimethylammonium salt wherein at least one of said alkyl radicals is an n-alkyl radical containing at least six carbon atoms.

8. An adduct of urea and dimethyldilaurylammonium bromide.

9. An adduct of urea and benzyldimethylaurylammonium chloride.

10. An adduct of urea and benzyldimethylauryloxymethylammonium chloride.

11. An adduct of urea and benzyldimethylaurylthiamethylammonium chloride.

12. An adduct of urea and lauryltrimethylammonium chloride.

13. In a method for separating quaternary dimethylammonium compounds according to structural configuration from a mixture thereof, said mixture comprising a quaternary ammonium compound (I) having as substituents on the nitrogen atom thereof (1) at least one straight-chain organic radical containing at least five methylene groups and (2) an aliphatic radical containing not more than one carbocyclic substituent, said carbocyclic substituent containing not more than six carbon atoms in the ring, said mixture further comprising at least one quaternary ammonium compound (II) of another type, and said mixture being substantially free from components containing functional groups reactive with urea, the steps which comprise contacting said mixture with urea and a urea solvent and separating from the resulting reaction mixture a solid, non-hygroscopic adduct of urea and said quaternary ammonium compound (I), substantially free from said quaternary ammonium compound (II).

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