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PREPARATION OF STABLE, SOLID, WATER-SOLUBLE, SURFACE-ACTIVE COMPOSITIONS CONTAINING UREA AND A QUATERNARY AMMONIUM COMPOUND

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This invention relates to improvements in granular, water-soluble, surface-active compositions containing effective proportions of water-soluble, surface-active quaternary ammonium compounds.

A large number of water-soluble, surface-active quaternary ammonium compounds are known. In general, these compounds are substituted ammonium salts in which all four of the hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of eight to sixteen carbon atoms. While it is possible to produce such water-soluble, surface-active quaternary ammonium compounds which are solids at ordinary atmospheric temperatures, the cost of the special raw materials required makes the cost of such compounds prohibitive in terms of commercial application. Further, although such compounds may be described as "solids," they frequently exhibit an oiliness or greasiness which causes them to agglomerate rapidly when originally flaked or granulated.

For example, coconut oil is a low cost raw material for the production of a particularly valuable group of such quaternary ammonium compounds, the distribution in length of the carbon chains of the constituent fatty acids being such that the quaternary ammonium compounds formed by conversion of the mixed fatty acids to amines followed by methylation and reaction with benzyl chloride are unusually effective surface-active and bactericidal agents. However, even when substantially anhydrous, these compounds are normally either an oily liquid or a greasy solid.

Other known water-soluble, surface-active quaternary ammonium compounds include lauryl dimethyl benzyl ammonium chloride, cetyl trimethyl ammonium bromide, heptadecyl trimethyl ammonium chloride, lauryl pyridinium chloride, octadecyl pyridinium bromide, decyl chlorobenzyl diethyl ammonium chloride, undecyl benzyl diethyl ammonium bromide, and the like.

These quaternary ammonium compounds are effective in dilutions of as little as 1%, 1/100% or even 1/1000%, for example in sanitizing vessels and utensils used in connection with food and drink, and are commonly used in aqueous solutions of such concentrations. For this reason, and the further reason that they are conveniently prepared in aqueous solution, these compounds are commonly manufactured and distributed as aqueous solutions containing from about 10% to about 50% of the quaternary ammonium compound.

In general, the ultimate consumer would prefer, for a variety of practical reasons, to receive such quaternary ammonium compounds as a granular solid, but for the oily or greasy characteristic previously mentioned. Further, since these compounds depress the freezing point of

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their solutions very little, containers in which such aqueous solutions are shipped, stored or handled must be protected against freezing to avoid losses resulting from resultant container damage. Of course, any such solid product must be of the same order of solubility as the quaternary ammonium compound itself if its practical value is to be maintained.

This problem has been recognized for some time and various expedients for dealing with it have been suggested. Probably the most effective of such proposals has been that of fusing the quaternary ammonium compound with urea. In some proportions, reasonably dry solids can be thus prepared but a fusion temperature upwards of about 110°-115° C. is usually required to obtain a homogeneous product and such temperatures initiate a curious decomposition that continues for an indefinite period even after the fusion is solidified and cooled to ordinary atmospheric temperatures. Such decomposition not only involves substantial losses of the effective agent but also renders the product objectionable during handling and in use.

Proposals involving the admixture of some inorganic salt with the quaternary ammonium compound, to take up any water present, have been less than successful for the reason that the difficulties involved are not to be solved merely by removing or binding the water present. The product remains an oily or greasy product tending to agglomerate.

This invention relates particularly to improvements in granular, water-soluble, surface-active compositions containing effective proportions of a water-soluble, surface-active quaternary ammonium compound and urea.

A mixture of urea in major proportion and such quaternary ammonium compounds in minor but effective proportion can be fused to produce a homogeneous melt, but the temperature required to obtain a homogeneous fusion from such simple mixtures usually exceeds 110°-130° C. and such temperatures initiate the curious decomposition previously mentioned. The decomposition products include ammonia and more odoriferous reaction products and the decomposition reaction, once initiated, continues with evolution of such decomposition products for a long period. This decomposition is not arrested by cooling and solidifying the fusion or melt.

We have discovered that mixtures of urea and 3%-22% by weight on the urea of such water-soluble, surface-active quaternary ammonium compounds can be heated to temperatures as high as 140°-150° C. to produce a homogeneous melt without initiating the decomposition previously mentioned provided a small proportion of a non-oxidizing acid not more volatile than acetic acid is present during fusion and provided the proportion of urea does not exceed 95% by weight on

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the total composition. The lowest temperature producing a homogeneous melt should be used. The acids we have found particularly advantageous are acetic acid, phosphoric acid and sulfuric acid. Of these, we prefer acetic acid. The proportions required approximate 2%-12% by weight on the total of urea and quaternary ammonium compound. The action of the acid appears to be more complex than simple neutralization of ammoniacal decomposition products. Even with the acid present, such decomposition products are usually evolved during fusion if the temperature much exceeds 115° C. And stability with respect to this decomposition is not attained by adding the acid to the product if, during fusion, the decomposition is initiated. Thus, the process of our invention comprises fusing together urea and about 3%-22% by weight on the urea of the water-soluble, surface-active quaternary ammonium compound, at a superatmospheric temperature for example of 110°-150° C., in the presence of about 2%-12% by weight on the total of urea and quaternary ammonium compound of such an acid. Following fusion, the melt is cooled and solidified. The product may be flaked or granulated as it solidifies or the solidified melt may be ground.

The granular product of our invention comprises urea, but not more than 95% by weight on the total product of urea, about 3%-22% by weight on the urea of a water-soluble, surface-active quaternary ammonium compound and about 2%-12% by weight on the total of urea and quaternary ammonium compound of, for example, acetic acid, phosphoric acid or sulfuric acid, and it may contain as much as 20% by weight on the total of urea, quaternary ammonium compound and acid of water. The quaternary ammonium compound may be supplied to the fusion operation, for example, as an aqueous solution containing 50% by weight of the quaternary ammonium compound. The direct product of such fusion, will, within the stated limits, be stable solids. Or, the quaternary ammonium compound may be dehydrated, partially or to substantially anhydrous condition before being supplied to the fusion operation. Again, the melt produced by fusing a concentrated aqueous solution of the quaternary ammonium compound with the urea and sodium acetate may be dehydrated after solidification. In any dehydration of the quaternary ammonium compound or products containing them, temperatures involving decomposition are to be avoided. One particularly advantageous product of our invention comprises urea, but not more than about 95% by weight on the total product of urea, about 3%-22% by weight on the urea of a water-soluble, surface-active quaternary ammonium compound, about 2%-12% by weight on the total of urea and quaternary ammonium compound of, for example, acetic acid, phosphoric acid or sulfuric acid, and about 10%-20% by weight on the total of urea, quaternary ammonium compound and acid of water. For many purposes, however, the proportion of water may be 4%-1% or less.

The practice and products of our invention will be illustrated by the following examples. In these examples, all parts are parts by weight.

Example I

A water-soluble, surface-active quaternary ammonium compound was derived from cocoanut oil fatty acids, by conventional processing, by conversion of the fatty acids to the corresponding cocoa amines, methylation to form dimethyl cocoa amines and treatment with benzyl chloride to

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produce cocoa dimethyl benzyl ammonium chloride in the form of a 50% by weight aqueous solution.

A series of compositions were prepared each containing 20 parts of this aqueous solution, proportions of glacial acetic acid varying from nothing to ten parts and that proportion of urea required to bring the total to 100 parts and each was fused to a clear homogeneous melt at a temperature of 135°-140° C. Ammoniacal decomposition products were in each instance evolved during the fusion. The melt was then cooled and solidified and the solid product was examined for evolution of ammoniacal decomposition products over a long period with the following results:

Proportions				Ammoniacal Decomposition Product Evolved
Urea	Quaternary Ammonium Compounds	Water	Acetic Acid	
80	10	10	0	Yes.
70	10	10	10	No.
75	10	10	5	No.
77	10	10	3	No.
78	10	10	2	No.
78.5	10	10	1.5	Yes.
79	10	10	1	Yes.

Example II

The procedure was the same as in the first example except that substantially all of the water had been removed from the quaternary ammonium compound by vacuum dehydration before it was supplied to the fusion. The results were as follows:

Proportions			Ammoniacal Decomposition Product Evolved
Urea	Quaternary Ammonium Compounds	Acetic Acid	
90	10	0	Yes.
85	10	5	No.
87	10	3	No.
88	10	2	No.
88.5	10	1.5	Slight.
89	10	1	Slight.

Example III

The procedure and materials used were the same as in the first example except that sulfuric acid (93.5% H₂SO₄) was substituted for acetic acid. With proportions of sulfuric acid upwards of about 2%-3% by weight on the total of urea and quaternary ammonium compound, there was no evolution of ammoniacal decomposition products.

Example IV

20 parts of an aqueous solution containing 50 parts by weight of lauryl pyridinium chloride, 75 parts of urea and 5 parts of syrupy phosphoric acid were fused to a clear homogeneous melt at a temperature of 135°-140° C. and the fusion was cooled and solidified. The solid product did not evolve ammoniacal decomposition products.

Other materials may be compounded with the product of our invention. For example, other surface-active materials such as sodium lauryl sulfate, potassium mono-naphthalene sulfonate and alkyl aryl polyether alcohols, and alkylol amides, sodium carbonate, sodium bicarbonate, normal and acid orthophosphates, polyphosphates such as triphosphate and tetraphosphate, polymetaphosphates, pyrophosphates and bo-

rates including borax may be included in the composition.

The process of our invention is, in a broader aspect, applicable to the production of homogeneous, solid products comprising urea and such water-soluble, surface-active quaternary ammonium compounds in cast shapes, for example, rather than in granular form. If the product is not to be granular, the proportions of quaternary ammonium compound on the urea may be varied over wider limits than those previously stated for granular products. For the production of such non-granular solid products, the proportion of the quaternary ammonium compound may range from 3% to 45% by weight on the urea.

We claim:

1. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 45% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of an acid selected from the group consisting of glacial acetic acid, syrupy phosphoric acid and concentrated sulfuric acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

2. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 22% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of glacial acetic acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

3. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 22% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of syrupy phosphoric acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

4. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges

by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 22% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of concentrated sulfuric acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

5. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 45% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of glacial acetic acid at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

6. A method of compounding stable, solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 45% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of syrupy phosphoric acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

7. A method of compounding solid, water-soluble, surface-active compositions which comprises fusing together the materials listed below in proportions within the indicated ranges by weight: a major proportion of urea in an amount not exceeding 95% of the total composition, 3% to 45% based on the weight of the urea of a water-soluble, surface-active quaternary ammonium salt in which all four hydrogens of the ammonium radical are substituted by organic radicals at least one of which contains a chain of 8 to 16 carbon atoms and 2%-12% based on the total weight of the urea and the quaternary ammonium compound of concentrated sulfuric acid, at superatmospheric temperature of about 110°-150° C. and cooling and solidifying the resulting melt.

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

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