Patented July 28, 1942

2,291,519

UNITED STATES PATENT OFFICE

2,291,519

PROCESS FOR PREPARING ACYLAMINO-METHYL QUATERNARY AMMONIUM COMPOUNDS

Walter Valentine Wirth, Woodstown, N. J., and Robert Freeman Deese, Jr., Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application June 13, 1941, Serial No. 397,902

4 Claims. (Cl. 260—295)

This invention relates to an improved process for preparing quaternary ammonium compounds possessing a long-chain acyl amido radical in their structure. More particularly, this invention relates to the production of compounds of the general formula

$$R—CONH—CH_2N(C_5H_5)—X$$

wherein R is an alkyl radical having from 8 to 20 carbon atoms in its structure X is the anion of a water-soluble acid, while $N(C_5H_5)$ represents the pyridine ring. Compounds of the above type are useful as water-repellency agents, that is, reagents for rendering textile fibers water repellent. (See British Patent No. 477,991 and U. S. Patent No. 2,146,392.)

It is an object of this invention to provide an improved process for preparing compounds of the above type in good yield and in a high state of purity. Other important objects of this invention will appear as the description proceeds.

In our earlier U. S. Patent No. 2,212,654, issued August 27, 1940 we have described an improved process for manufacturing compounds of the above type. Said process in its essentials consisted of reacting a higher acyl amide, for instance stearamide, with paraformaldehyde in an inert organic liquid, in the optional presence of pyridine, to produce the corresponding methylol-amide, for instance stearamido-methanol. Then, without isolating the intermediate methylol-amide, further quantities of pyridine were added if necessary, and dry hydrogen chloride was fed into the mixture to form pyridine-hydrochloride within the mass. The mass would then be heated to a temperature of about 50 to 80° C. to effect a reaction as indicated by the following equation:

$$R—CONH—CH_2OH+N(C_5H_5)\cdot HCl \rightarrow R—CONH—CH_2—N(C_5H_5)—Cl+H_2O$$

As inert organic liquids for the first part of the reaction the following types were suggested: hydrocarbons, as typified by benzene hexane and certain petroleum factions ketones, as typified by acetone and methyl-ethyl-ketone; and miscellaneous non-hydroxylic solvents as typified by ethylene chloride. These solvents have been found to give very desirable improvements in yield and quality of the product, and have in general improved the economy of the process. Nevertheless, when manufacturing is done on a commercial scale, it is found that some of these solvents possess special characteristic disadvantages which though not fatal to the process nevertheless point to the desirability of further improvement.

Thus when ketones are employed as the liquid dilutent, it is found that the yield of the desired quaternary compound is not quite so high as when hydrocarbon solvents are employed. Furthermore, the product is discolored by comparison with the product obtained when a hydrocarbon solvent is employed. Apparently, the hydrocarbon solvents have the power to hold in solution (and eventually filter out) certain by-product impurities which solvents of the ketone type do not completely dissolve.

On the other hand, the use of a hydrocarbon, although giving a product of highest yield and purity has the disadvantage of slow filtration. It will be noted that in the final step of manufacture, the solid stearamido-methyl-pyridinium chloride produced is usually separated from the solvent (and by-product impurities dissolved therein) by filtration. For some reason, however, the hydrocarbon type solvent clings tenaciously to the crystals of the quaternary compound, and filtration is so slow that it will often take days and even weeks to produce a product of the same relative "dryness" (i. e., freedom from solvent), as may be produced in a few hours where acetone or ethyl-methyl ketone is the solvent.

It has been found that the slight deficiency in yield in the case of a ketone solvent can be overcome sometimes by using in the second step a larger excess of pyridine hydrochloride. But this is objectionable not only from the viewpoint of economy of materials but also because the excess pyridine hydrochloride generally stays in the final product, reducing its percentage purity. Furthermore, pyridine hydrochloride tends to tender the fabric eventually treated with the product, and it is therefore obviously undesirable to increase the proportion thereof in the final product.

It is clear from all the above that the choice and adaptation of solvent for the process in question is not so simple as might appear at first thought, and that commercial manufacture imposes on the process problems which would not occur or would not be material in pure scientific research.

Now according to our present invention the above economical problem of choice of solvent has been solved successfully by the employment of a combination of solvents preferably in a particular sequence. More particularly, we have found it advantageous to carry out the first step of the process, that is methylol formation, in a

hydrocarbon solvent, and then adding a low boiling ketone solvent to the second stage of the process, that is the quaternization step. The requisite tertiary base, such as pyridine, may be added either in the first step, or in the second step, or partially in each step. The hydrogen chloride is fed-in during the second step, and in all other details the process may follow the procedures set forth in our prior patent above referred to.

Some improvement may also be obtained by using initially a mixed solvent consisting of a liquid hydrocarbon and a liquid ketone. But the results are not so good as with the successive arrangement above indicated. Likewise, improved results may also be obtained by using a hydrocarbon solvent exclusively in both stages of the process only adding a liquid ketone just prior to filtering. But this process requires the use of a larger quantity of the hydrocarbon solvent to maintain the mass in stirrable state throughout the process. Hence this alternative is not so economical as the preferred process above indicated.

The theory of this surprising effect is not entirely clear to us. It is possible that the water formed in the quaternization step has some influence on the rate of filter-ability of the hydrocarbon solvent, and that the ketone by absorbing this water diminishes its inhibiting effect on the filtration. It will be noted that the low boiling liquid ketones which would naturally be available for our purpose, for instance acetone, diethyl ketone or methyl-propyl-ketone, are at least partially miscible with water. However, the theory of the observed phenomena are not essential to the successful practice of our invention, and we therefore do not desire to limit this invention to any particular theory. It is surprising in any event, that the use of two solvents as indicated overcomes the disadvantages observed with each solvent individually. It is not often in chemistry that two reagents can be made to complement each other and compensate for each other so perfectly.

Without limiting this invention, the following examples are given to illustrate our preferred mode of operation. Parts mentioned are by weight.

Example 1

114 parts of stearamide, 45 parts of pyridine, 18 parts of paraformaldehyde and 150 parts of toluene were mixed and held 12 hours at 75 to 80° C. The mass was cooled slowly to 25° C. and a fairly stiff paste resulted. 150 parts of acetone was added and the whole stirred until a smooth slurry resulted. Dry hydrogen chloride was passed into the mass at about 30° C. until the charge was acid. 10 parts more of pyridine was added and the charge held at 60 to 65° C. for four hours after which it was cooled to about 15° C. and filtered. Very rapid filtration resulted. The wet cake was dried and a high yield of crude stearamido methyl pyridinium chloride was obtained in a state of high purity and containing a relatively small proportion of pyridine hydrochloride.

Example 2

114 parts of stearamide, 45 parts of pyridine, 16 parts of paraformaldehyde and 150 parts of "Dependip" (a mixture of saturated hydrocarbons—90% boiling between 120 and 139° C.) were mixed and held six hours at 90 to 95° C. The reaction mass formed a stiff paste on cooling to about 30° C. 125 parts of diethyl ketone were added and the whole was agitated until a smooth slurry resulted. Dry hydrogen chloride was passed into the mass until it was acid. 10 parts more of pyridine were added. The reaction mass was then heated to 70° C., held at 70 to 75° C. for 2½ hours then cooled to 13° C. and filtered. The filtration was complete in ½ hour on a small Buchner suction funnel. After drying, the product was recovered in high yield, in a high state of purity and of relatively small pyridine hydrochloride content.

Example 3

276 parts of stearamide, 526 parts of "H–29" (a mixture of saturated aliphatic hydrocarbons—at least 80% boiling between 100 and 130° C.), 35.1 parts of paraformaldehyde and 88.8 parts of pyridine were heated at 75 to 80° C. for 10 hours and then cooled. Crystallization started at about 70° C. and a pasty mass was formed on cooling to about 25° C. 132 parts of acetone were then added, and a smooth slurry resulted. Dry hydrogen chloride was passed into the mass until it was acid to Congo Red test paper at 20 to 30° C. 22.2 parts of pyridine were then added and the charge was held at 60 to 65° C. for four hours. The charge was cooled to 12° C. over a period of about 18 hours and filtered. The filtration was complete in about an hour. The wet cake obtained was dried and gave a crude stearamido methyl pyridinium chloride of exceptionally high purity and of exceptionally low pyridine hydrochloride content.

Example 4

114 parts of stearamide, 45 parts of pyridine, 18 parts of paraformaldehyde and 150 parts of "Dependip" were agitated, heated to 75° C. and held at 75 to 80° C. for 12 hours. After cooling to room temperature the smooth slurry was diluted with 150 parts of methyl-n-propyl-ketone and acidified with dry hydrogen chloride. The excess acid was neutralized with 3 parts of pyridine, and 7 parts more of pyridine was added. The charge was heated to 70° C. and held at 70 to 75° C. for 2½ hours, after which it was cooled to 14° C. and filtered. The filtration was very rapid. Drying the press cake gave a product of high quality and good yield.

Example 5

114 parts of stearamide, 45 parts of pyridine, 18 parts of paraformaldehyde and 150 parts of "H–29" (boiling range 80 to 130° C.) were agitated and heated for 12 hours at 75 to 80° C. After cooling to 25° C., 150 parts of methylisobutyl-ketone was added. A thin slurry of the methylol stearamide was formed, into which dry hydrogen chloride was passed at 20 to 35° C. until the mass was acid to Congo Red. The excess acid was neutralized with 3 parts of pyridine and 7 parts excess pyridine was added. After heating at 70 to 75° C. for 2½ hours, the charge was cooled to 13° C. and filtered. The filtration was very rapid and resulted in a product of exceptionally high qualities and yield.

Example 6

114 parts of stearamide, 5 parts of pyridine, 18 parts of paraformaldehyde and 150 parts of "Dependip" were mixed and held for 17½ hours at 75 to 80° C. The methylol stearamide partially precipitated out. This hot slurry was then

added to 150 parts of methyl-ethyl-ketone containing pyridine hydrochloride (i .e., 45 parts pyridine + enough HCl to make the same acid to Congo Red) and 6 parts excess pyridine. After heating for 4 hours at 60 to 65° C. the charge was cooled to 13° C. and filtered. Rapid filtration resulted, and gave a good yield of high quality product.

The pyridine hydrochloride requisite for the above examples may also be formed by dissolving dry hydrogen chloride in the selected ketone, e. g., acetone, at 0 to 5° C. and then adding this ketone solution to the slurry of methylol stearamide in the mixture of pyridine and hydrocarbons.

As already mentioned, some improvement in both yield and purity of product may be obtained also by using initially a mixture of hydrocarbon and ketone. The following additional example illustrates this procedure.

Example 7

114 parts of stearamide, 18 parts of paraformaldehyde, 45 parts of pyridine, 150 parts of methyl-ethyl-ketone and 150 parts of "Dependip" were heated together and held for 10 hours at 75° to 80° C. The mass was cooled to 25° C. to form a smooth slurry. After acidifying with dry hydrogen chloride, 10 parts of pyridine was added to insure a neutral solution and the whole was heated for 4 hours at about 63° C. The mass was then cooled to 14° C. and filtered. The filtration was quite rapid, and gave a product of high qualtity and good color compared to the product obtained by using a ketone alone as solvent.

While the above examples have employed stearamide as initial material in each case, it will be clear that the same process may be applied also to other higher fatty acid amides, such as lauramide or palmitamide, to produce the corresponding acyl-amido-methylene-pyridinium chlorides in improved yield and quality. Likewise in lieu of the ketones specifically named, any other dialkyl ketone may be employed provided it is liquid within the range of temperatures employed (say 20 to 100° C.) and is at least partially miscible with water.

Many other variations will be apparent to those skilled in the art without departing from the spirit of this invention.

We claim:

1. The process of producing a quaternary ammonium compound of the general formula

$$R—CONH—CH_2—N(C_5H_5)—X$$

wherein R is an alkyl radical having at least 8 carbon atoms, X is the anion of a water-soluble acid, while $N(C_5H_5)$ designates the pyridine ring, which comprises first reacting the corresponding acyl amide of the formula $R—CONH_2$ with paraformaldehyde in an organic liquid medium consisting at least in part of a hydrocarbon solvent, then reacting the resulting mass with a pyridinium salt of the formula $N(C_5H_5)\cdot HX$ in the presence of free pyridine, and in the further presence of a liquid dialkyl ketone which is adapted to absorb the water of formation in the reaction mass.

2. A process of producing an acylamido-methyl-pyridinium halide of the formula

$$R—CONH—CH_2—N(C_5H_5)—Hal$$

wherein R stands for an alkyl radical having at least 8 carbon atoms, $N(C_5H_5)$ designates a pyridine ring, while "Hal" stands for halogen, which comprises reacting the corresponding acyl amide of formula $R—CONH_2$ with paraformaldehyde in a liquid medium consisting at least partly of a liquid hydrocarbon to produce in situ a methylol compound of the formula

$$R—CONH—CH_2OH$$

then adding to the reaction mass a liquid ketone which is at least partially water-miscible, and feeding dry hydrogen halide into the reaction mixture after having added pyridine to the reaction mass at least during one of the above two stages.

3. A process of producing an acylamido-methyl-pyridinium chloride, whereof the acyl group contains at least 8 carbon atoms, which comprises reacting the corresponding acylamide with paraformaldehyde in a liquid medium consisting essentially of a liquid hydrocarbon and pyridine, then adding to the reaction mass a liquid dialkyl ketone and such further quantities of pyridine as may be necessary to bring up the total quantity of pyridine in the mass to at least one mole per mole of acylamide initially employed, feeding in dry hydrogen chloride to form pyridine-hydrogen-halide in the reaction mass, adding an excess of pyridine, warming the reaction mass to effect reaction between the intermediate acylamido-methylol compound and the pyridine-hydrogen-halide, and isolating the solid reaction product by filtration.

4. A process of producing stearamido-methyl-pyridinium chloride, which comprises reacting stearamide with paraformaldehyde in a medium consisting essentially of a liquid hydrocarbon containing sufficient pyridine to provide at least one mole of pyridine per mole of initial stearamide; then adding to the reaction mass a liquid dialkyl-ketone adapted to absorb the water of formation in the subsequent quaternization step; feeding in hydrogen chloride until the mass assumes substantially an acid reaction; neutralizing the excess acidity with further quantities of pyridine, warming the reaction mass to a temperature of about 60 to 75° C., and filtering off the solid reaction product thus obtained.

WALTER VALENTINE WIRTH.
ROBERT FREEMAN DEESE, JR.