3,180,870

ART OF PROMOTING CRYSTAL GROWTH

Penn F. Spitzer, Jr., South Bound Brook, and Oscar L. Burgenson, Jr., New Market, N.J., assignors to American Cyanamid Company, New York, N.Y., a corporation of Maine

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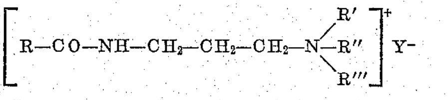
This invention relates broadly to the art of promoting the crystal growth of crystallizable organic materials. More particularly it is concerned with the use in this art of a crystal-growth promoter comprising a quaternary ammonium compound represented by the general formula

I



$$\left[R{-}CO{-}NH{-}CH_2{-}CH_2{-}CH_2{-}\overset{R'}{\underset{R'''}{N}}{-}R''\right]^{+}Y^{-}$$

wherein R represents a member of the group consisting of aliphatic and alicyclic radicals containing at least 7 carbon atoms, R′ and R″ each represent a member of the group consisting of alkyl and hydroxyalkyl radicals containing from 1 to 5 carbon atoms, inclusive, R‴ represents a member of the group consisting of alkyl, hydroxyalkyl, alkenyl and aralkyl radicals, and Y represents an anion.

Illustrative examples of radicals represented by R in Formula I are heptyl, octyl, octenyl, nonyl, nonenyl, decyl, decenyl, undecyl, undecenyl, tridecyl, tetradecyl, tetradecenyl, heptadecyl, heptadecenyl, octadecyl, octadecenyl, the residue of abietic acid, etc. Illustrative examples of radicals represented by R′ and R″ are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, tert.-butyl, n-amyl, isoamyl, sec.-amyl, tert.-amyl and the other isomeric amyl radicals, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, dihydroxypropyl, hydroxybutyl, dihydroxybutyl, hydroxyamyl, dihydroxyamyl, etc. Illustrative examples of radicals represented by R‴ are the same alkyl and hydroxyalkyl radicals as those given with reference to R′ and R″ and, in addition, the higher alkyl radicals, e.g., hexyl to octadecyl, inclusive, the mono-, di-, tri- and higher hydroxy derivatives of the aforementioned higher alkyl radicals (i.e., hexyl to octadecyl, inclusive); the same alkenyl radicals as those given above with reference to R and, also, allyl, methallyl, ethallyl, 2-butenyl, 3-buteny, 3-methyl-2-butenyl, 3-pentenyl, 4-pentenyl, 2,3-pentadienyl, 3-methyl-3-butenyl and the higher alkenyl radicals, e.g., hexenyl to octadecenyl, inclusive; and the various aralkyl radicals, e.g., benzyl, phenylethyl, phenylpropyl, phenylisopropyl, phenylbutyl, etc. Illustrative examples of anions represented by Y are the halide ions (that is, Y can represent a chloride, bromide, fluoride or iodide), sulfate, sulfonate, phosphate (more particularly dihydrogen phosphate), hydroxide, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate, acetate and the other common inorganic and organic anions.

Quaternary ammonium compounds of the kind used in practicing the present invention are disclosed in, for instance, Carnes U.S. Patents 2,626,876 and 2,626,877. Reference also is made to Cook et al. U.S. Patent 2,589,674 which discloses how compounds used in practicing this invention can be prepared, and wherein are claimed a sub-class and certain species of quaternary ammonium compounds that are useful in carrying the present invention into effect.

A more specific embodiment of the present invention is the improvement, in the removal by filtration of finely-divided particles of organic material from an aqueous suspension or slurry containing said particles, which comprises adding to a solution, containing a crystallizable organic material capable of crystallizing from said solution, at least about 0.1% (e.g., from 0.1 to 10% or more) by weight, based on the dry weight of the said crystallizable organic material, of a crystal-growth promoter comprising or consisting essentially of a quaternary ammonium compound of the kind embraced by Formula I. The upper limit of the amount of the quaternary ammonium compound employed is not critical. It may be, by weight, about 0.2%, or 0.5%, or 1%, or as much as about 2 or 3% or even 5% or 10% or more, based on the dry weight of the crystallizable organic material. No advantages appear to accrue from the use of more of the quaternary ammonium compound than is necessary to provide the desired crystal growth and the accompanying improvement in filterability of the aqueous suspension of the particles or crystals of organic material, as well as the other advantages hereinafter set forth. The use of any excess of the defined crystal-growth promoter above that needed to secure the desired results seems to be wasted and only adds to the cost of the process.

In industrial chemical operations it is often necessary to filter solid suspended material from aqueous suspensions. When particles are very finely divided, difficulty is often encountered in such filtration. In some instances, particles are so finely divided that they pass through the filtering medium; or, the size of the particles may be such that the filtering cloth or other medium becomes plugged, thereby reducing the rate of filtration so that excessive time is required for this operation; or, filtration may not be carried out completely, resulting in a very wet or sloppy filter cake. Further difficulties may be caused, in addition to loss of material and slow filtration, in that processing of the sloppy or mushy filter cakes may be extremely difficult and more costly.

The present invention is based on our discovery that, by adding a cationic quaternary ammonium compound of the kind embraced by Formula I to a liquid mass or solution (more particularly an aqueous liquid mass or solution) containing a crystallizable organic material or compound, crystal growth surprisingly is promoted. Consequently, in subsequent filtration operations filtration is improved, and difficulties arising from loss of material, excessive filtering periods and sloppy or mushy filter cakes are avoided.

It was most surprising and unexpected that compounds of the kind embraced by Formula I should be capable of acting as crystal-growth promoters and should provide such excellent and non-obvious results. Such effects are not obtained generally with surface-active agents of various types including cationic, anionic and nonionic agents. To the best of our knowledge and belief the improvement is specific with respect to the particular class and species of cationic agent used in practicing the present invention. The aforementioned Carnes patents disclose the use of quaternary ammonium compounds defined by Formula I as antistatic agents, specifically for shaped articles comprising a vinyl resin; while the aforementioned Cook et al. patent discloses their use as wetting agents, detergents, emulsifying agents, germicides and fungicides. Hence it would not be expected and in no way could have been predicted that, by the use of an agent which has dispersant properties, crystal growth of a crystallizable organic material would be promoted and in consequence of which the improved filtration effects herein described would result.

The present invention should not be confused with any prior suggestions of the use of a compound embraced by Formula I as a settling agent that is applied to various insoluble slimes, including bacterial suspensions as well as chemical and mineral substances, and wherein the addition of as little as 10 parts per million of the quaternary ammonium compound may cause rapid settling of the suspended substance. To the best of our knowledge and belief such suggested use of the quaternary ammonium compounds embraced by Formula I as settling agents was not applied to, and was not known to be applicable to, crystallizable (or potentially crystallizable) organic materials of the kind with which this invention is concerned. As is well known to those skilled in the art, a suggestion of "settling" a particular organic material is entirely different from a teaching of imparting crystal-growth characteristics to a crystallizable (or potentially crystallizable) organic material, and a teaching or a suggestion with respect to the one is in no sense of the word a teaching or a suggestion with respect to the other.

Illustrative examples of organic materials, more particularly crystallizable (including potentially crystallizable) organic materials, that can be modified in accordance with this invention to promote their crystal growth and thereby improve the filterability of aqueous suspensions or slurries of the thusly modified organic material are:

2-aminodiazine bisulfite
Ferrous calcium citrate
Acetylsulfanilyl chloride

Other examples of crystallizable and potentially crystallizable organic materials to which the present invention is applicable will be apparent to those skilled in the art from the foregoing illustrative examples.

The invention may be illustrated by the method and results obtained in the use of compounds of the kind embraced by Formula I in the manufacture of 2-amino-1,3-diazine bisulfite, which is the bisulfite product of 2-aminopyrimidine and hereafter is designated for brevity as 2-aminodiazine bisulfite or, merely, as aminodiazine bisulfite. The compound is an intermediate in the manufacture of 2-aminodiazine (2-aminopyrimidine), which is an intermediate for making sulfadiazine, a well-known sulfa drug.

This process involves the filtration of a suspension of aminodiazine bisulfite. Under ordinary circumstances this filtration step is extremely difficult, requiring excessive periods of time with loss of material and involving sloppy and mushy filter cakes, which are difficult to wash and costly to process.

In practical plant operation of a process for making 2-aminodiazine (hereafter for brevity sometimes designated as aminodiazine), the 2-aminodiazine reaction mixture is "drowned" in water. The 2-aminodiazine, prepared in any convenient manner, is isolated from the drowned reaction mixture containing process salts, unused reactants, by-product material, etc., by first neutralizing the aqueous solution with ammonia followed by treatment of this solution with sulfur dioxide, which causes precipitation of 2-aminodiazine bisulfite. This aqueous suspension is subjected to filtration, giving a filter cake of aminodiazine bisulfite. To isolate 2-aminodiazine, this bisulfite compound is treated with concentrated aqueous ammonia thereby to obtain, at 60° C., a solution of 2-aminodiazine. The 2-aminodiazine is crystallized from this solution by cooling and is removed by filtration, thus isolating the desired solid 2-aminodiazine.

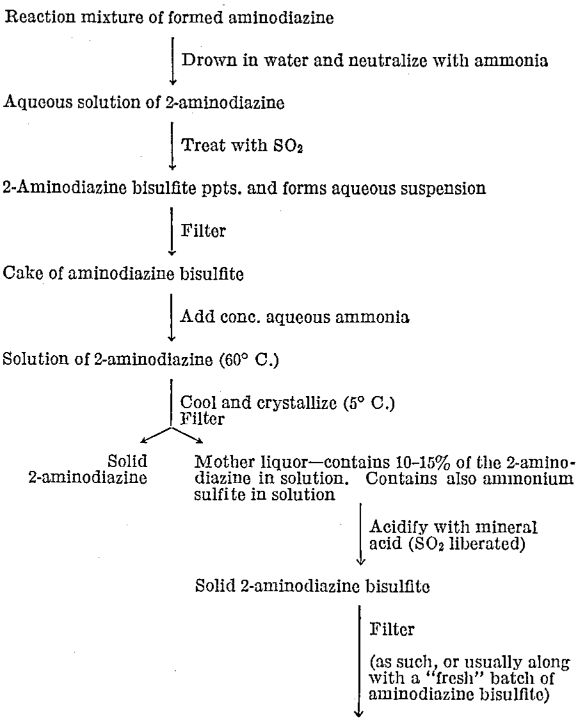
The mother liquor from this 2-aminodiazine filtration contains a substantial amount (e.g., from about 10 to 15% by weight of the total end-product) of 2-aminodiazine, and excess ammonia in aqueous solution. The solution also contains ammonium sulfite. To recover the 2-aminodiazine from this mother liquor, the mother liquor containing dissolved 2-aminodiazine is acidified with a mineral acid, e.g., HCl, H_2SO_4, etc. Ordinarily plant by-product mineral acid is used, for instance acid mother liquor from the precipitation of acetylsulfanilyl chloride containing sulfuric and hydrochloric acids. This acidification liberates SO_2 which, in turn, converts the 2-aminodiazine in the reaction mass to 2-aminodiazine bisulfite. This mixture is then filtered to recover the 2-aminodiazine bisulfite. This may be filtered as such or generally, in commercial practice, along with a "fresh" batch of aminodiazine bisulfite. It is this filtration of 2-aminodiazine bisulfite either alone or in combination with the fresh aminodiazine bisulfite where extreme difficulty is encountered, e.g., loss of material, long filtration periods, sloppy filter cakes, etc. In addition, it frequently happens that acidification of aminodiazine mother liquor results in suspensions wherein the solid is so fine that the milky suspension passes completely through the filter cloth and the filter paper, resulting in a total loss of recoverable product amounting to from about 10 to 15% of the total weight of product that should be obtained.

By the addition of at least 0.1% and preferably from 0.2 to 1.5% by weight of a quaternary ammonium compound of the kind embraced by Formula I to the 2-aminodiazine mother liquor before acidification, which weight is based on the dry weight of the aminodiazine present therein, the filterability of the suspension containing the crystalline 2-aminodiazine bisulfite is improved due to its larger particle size; the yield of recovered 2-aminodiazine bisulfite is increased; and the aforementioned difficulties are obviated. The quaternary ammonium compound employed in practicing the present invention is usually added as the commercially available 50% solution in an isopropyl alcohol-water mixture.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

The procedure for the preparation of 2-aminodiazine bisulfite and conversion to 2-aminodiazine as described above may be outlined as follows:



(A) When the procedure is carried out as outlined,

(1) The filtration time for filtration of the aminodiazine bisulfite in a batch size for about 635 lbs. of aminodiazine varies from about 4 to 16 hours;

(2) An amount in excess of 30–35 lbs. of aminodiazine

bisulfite per batch is lost (occasionally as high as 60–70 lbs.);

(3) A sloppy filter cake of 2-aminodiazine bisulfite, consistency of about thick pea soup with considerably retained acid liquor, is obtained; and

(4) The retention of large amounts of acidic mother liquor in the sloppy cake requires excessive aqua ammonia usage in converting to aminodiazine with resultant increase in batch volume, decreasing aminodiazine isolated because of solubility in larger volume of liquor, increase in recovery and recycling problems, and cost increases due to losses, additional raw materials and labor.

(B) When about 3–5 lbs. of a 50% solution in a 50–50 isopropanol-water mixture of stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate is added to the aminodiazine mother liquor (containing 60–90 lbs. of aminodiazine in a total of 3500 lbs. of total solution), improved results are obtained as follows:

(1) The filtration time of the aminodiazine bisulfite is reduced from about 4 to 16 hours per batch to less than 1 hour per batch.

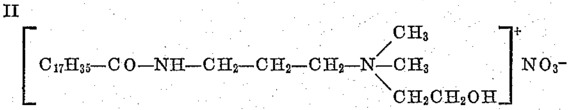
(2) There is a minimum improvement in the yield of aminodiazine of 30–35 lbs. per batch (batch size average about 635 lbs.), and the elimination of the occasional 60–70 lb. losses.

(3) There is obtained a dry, sandy filter cake of aminodiazine bisulfite having very little retained moisture. It is readily handled, thereby reducing labor costs, and is capable of complete washing without any difficulty. There is no retention of acid solution and it may be converted to aminodiazine with improved results, e.g., reduced ammonia usage, due to less retaining acid, lower volume, etc.

By the improved method, there is obtained a coarse, harder crystal of aminodiazine bisulfite which filters rapidly, gives a dry cake with little loss of material.

Instead of using stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate, the formula for which is

II



$$\left[C_{17}H_{35}-CO-NH-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_2CH_2OH}{N}}-CH_3\right]^+ NO_3^-$$

as described under B of Example 1, essentially the same results are obtained by employing an equivalent amount of any other compound (or mixture of compounds) embraced by Formula I, specifically one or more of the following:

A caprylamidopropyl dimethyl beta-hydroxyethyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate (dihydrogen phosphate).

A stearamidopropyl dimethyl dihydroxypropyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A stearamidopropyl tris(beta-hydroxyethyl) ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A lauramidopropyl methyl bis(beta-hydroxyethyl) ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

An abietamidopropyl dimethyl (beta-hydroxyethyl) ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A stearamidopropyl dimethyl benzyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A myristamidopropyl dimethyl benzyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A caprylamidopropyl dimethyl benzyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A stearamidopropyl trimethyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A myristamidopropyl trimethyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

A palmitamidopropyl trimethyl ammonium salt, e.g., chloride, nitrate, sulfate, phosphate.

Also, the quaternary ammonium compounds identified by their formulas in column 4, lines 3 to 68, inclusive (Formulas IV through XVI) of the aforementioned Carnes U.S. Patent 2,626,877.

EXAMPLE 2.—PREPARATION OF FERROUS CALCIUM CITRATE

(A) Under an inert atmosphere, e.g., gaseous nitrogen, 700 parts of water is mixed with 100 parts calcium carbonate, 11.6 parts powdered iron, and 3 parts concentrated hydrochloric acid. To the mixture is then added 153.7 parts citric acid, after which it is stirred at 100°–102° C. for 6 hours. After cooling to 25° C. the product, ferrous calcium citrate, is isolated by filtration, washed and dried.

The filtration proceeds slowly and materially increases the cost of the process. Also, the product dries with difficulty to very fine crystals with poor flow qualities.

(B) The same procedure is followed as described under (A) with the exception that, in one case, one part of stearamidopropyl dimethyl β-hydroxyethyl ammonium phosphate (dihydrogen phosphate) and, in another instance, one part of stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate is added to the reaction mixture before heating the same.

In both cases, and unlike the results obtained in the absence of the quaternary ammonium compound, the resulting product can be filtered rapidly from the reaction mass. Furthermore, the washed product yields, after drying, large granular crystals with free-flowing characteristics.

Similar results are obtained when the corresponding sulfate or chloride is used in place of the particular quaternary ammonium salts used in the (B) portion of this example.

If desired, one can effectively use any other quaternary ammonium compound of the kind embraced by Formula I instead of the aforementioned stearamidopropyl dimethyl β-hydroxyethyl ammonium compounds.

EXAMPLE 3.—ISOLATION OF ACETYLSULFANILYL CHLORIDE

When acetylsulfanilyl chloride is isolated from suspensions thereof by filtration there are obtained, using the prior techniques, very fine particles averaging less than 1 to 2 microns and with only a relatively few agglomerates averaging as large as 15 microns. However, when the product before isolation is crystallized from a liquid medium or mass containing about 0.5% of stearamidopropyl dimethyl β-hydroxyethyl ammonium phosphate or nitrate, the particle size is increased and a coarse, granular material ranging from 100 to 2400 microns in size is obtained. Most of the particles, in number, are in the range of 100 to 600 microns; while most of the particles by weight are in the range of 600 to 2000 microns.

When surface-active agents different from those used in practicing this invention, more particularly surfactants identified opposite Nos. 1 through 19 of Table II of Example 4, the above-described improvement in crystal size is not obtained.

EXAMPLE 4

A study was carried out to ascertain the influence of various types of surfactants upon crystal formation and filtration effects. For this purpose, the mother liquor from the filtration of aminodiazine was used (see Example 1).

A large sample of the aforementioned mother liquor from a plant operation was divided into 400-part aliquots. To each aliquot was added 2 parts of surfactant. In the case of the stearamidopropyl dimethyl β-hydroxyethyl ammonium salts, specifically the nitrate and the phosphate (dihydrogen phosphate), as little as 0.5 part was used. The aliquot was acidified to a pH of 2 with a mineral acid, more particularly with an acidic mother liquor from the preparation of acetylsulfanilyl chloride and which contained both H_2SO_4 and HCl, with the H_2SO_4 being present in predominant amount. The aliquot was stirred for 45 minutes to complete the precipitation. The aminodiazine bisulfite was then removed by filtration. The time for filtration was noted and the product was dried and weighed.

The results with various agents, including the aforementioned quaternary ammonium salts, are shown in Table I. This table shows the yield of material obtained in grams and, also, the filtration rate. In addition, Table I includes measurements to show the crystal growth results with reference to particle size.

It is to be noted that greatly improved results are obtained by using quaternary ammonium salts of the kind embraced by Formula I (Nos. 20, 21 and 22 in the tables). The filtration rate with these agents is from 1 to 2 minutes, whereas with the other agents much longer times are required. In addition, the amount of aminodiazine bisulfite obtained from an aliquot portion is much greater, generally speaking, with the aforementioned compounds than with any of the other agents. When surfactant No. 7 was used, the amount of material isolated was relatively high, but the slow filtration rate with this surfactant would make it unsuitable for use. In a number of instances, the crystal size was improved as with surfactant No. 2 but the yield and filtration rates were unsatisfactory.

Table II identifies the surfactants studied by their chemical names and, also, by their ionic characteristics.

Table I

Surfactant	Yield, Grams	Filter Rate, Min.	Range, μ	Most No., μ	Most Wt., μ	Filter Cake Quality
1	1.2	6-7	<1-130	<1-10	20-30	Sticky and gummy.
2	5.5	4	10-600	10-100	100-600	Granular, fairly dry.
3	3.2	6	<1-200	<1-10	40-200	Dense hard cake.
4	5.6	4	10-150	10-80	80-150	Granular fairly dry.
5	8.2	5-6	2-300	2-50	50-300	Fine particle, hard cake.
6	5.9	5-6	<1-350	<1-100	100-350	Soft crystals, hard cake.
7	8.4	6-7	<1-150	<1-80	80-150	Very fine particle, hard cake.
8	4.5	8	----------	----------	----------	Sticky mass.
9	5.2	6-7	1-200	<1-60	60-200	Fine particle, hard cake.
10	5.0	7-8	----------	----------	----------	Sticky mass, soft crystals.
11	2.6	4-5	1-80	<1-5	5-80	Hard, dense cake.
12	6.1	4-5	10-150	10-80	80-150	Slightly granular, hard cake.
13	2.6	4-5	<1-40	<1-5	5-40	Very fine particle.
14	4.5	8	<1-150	<1-5	20-150	Sticky, discolored cake.
15	4.9	6-7	<1-100	<1-2	10-100	Fine particle, hard cake.
16	5.4	5-6	<1-160	<1-2	20-160	Slightly granular, hard cake.
17	4.4	8	<1-200	<1-2	20-200	Slightly granular, soft, sticky, discolored.
18	0		Could not filter			Soft, sticky mass.
19	4.9	8	<1-200	<1-2	20-200	Fine particle, sticky.
20 [1]	8.6	1-2	5-400	30-100	100-400	Granular, dry, free flowing.
21 [1]	8.4	1-2	5-350	5-100	100-350	Do.
22 [1]	8.3	1-2	5-350	5-100	100-350	Do.

[1] NOTE.—Quaternary ammonium compounds of the kind embraced by Formula I.

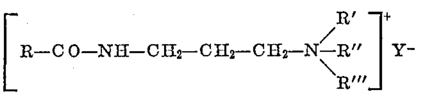
Table II

Surfactant	Chemical Class	
1	Alkyl aryl polyether alcohol	Nonionic.
2	Tertiary amines; ethylene oxide condensates with primary fatty amines.	Cationic.
3	Sodium alkyl sulfate	Anionic.
4	Tertiary amines; ethylene oxide condensates with primary fatty amines.	Cationic.
5	Polyoxyethylene sorbitan monolaurate	Nonionic.
6	Sorbitan monolaurate	Do.
7	Ethylene oxide condensate with condensate of propylene oxide and propylene glycol.	Do.
8} 9}	Sulfated and sulfonated fatty acid esters in mixture with aliphatic hydrocarbons.	Anionic.
10	Fatty alcohol amine sulfate	Do.
11	Polyoxyethylene-fatty compound condensate.	Nonionic.
12	Ethylene oxide condensate with condensate of propylene oxide and propylene glycol.	Do.
13	Pyridinium chloride	Cationic.
14	Alkyl aryl polyethylene glycol ether	Nonionic.
15	Dioctyl ester of sodium sulfosuccinic acid	Anionic.
16	Alkyl aryl ether	Nonionic.
17	Ethylene oxide-alkyl phenol condensate	Do.
18	Primary amine	Cationic.
19	Fatty alcohol phosphate compositions	Anionic.
20 [1]	Stearamidylpropyl dimethyl β-hydroxyethyl ammonium nitrate.	Cationic.
21 [1]	do	Do.
22 [1]	Stearamidylpropyl dimethyl β-hydroxyethyl ammonium dihydrogen phosphate.	Do.

[1] NOTE.—Quaternary ammonium compounds of the kind embraced by Formula I.

We claim:

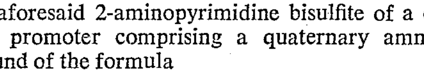
1. The method of promoting crystal growth of a crystallizable organic material selected from the group consisting of 2-aminopyrimidine bisulfite, ferrous calcium citrate and acetylsulfanilyl chloride, said method comprising adding to a liquid mass containing said organic material at least about 0.1% by weight, based on the dry weight of the said organic material, of a crystal-growth promoter comprising a quaternary ammonium compound of the formula



$$\left[\mathrm{R{-}CO{-}NH{-}CH_2{-}CH_2{-}CH_2{-}}\overset{R'}{\underset{R'''}{\mathrm{N}}}\mathrm{{-}R''}\right]^{+}Y^{-}$$

wherein R is a substituent selected from the group consisting of abietyl and aliphatic hydrocarbon having from 7 to 18 carbon atoms, inclusive, and wherein any unsaturation between adjacent carbon atoms is a double bond; R′ and R″ each is a substituent selected from the group consisting of unsubstituted alkyl having from 1 to 5 carbon atoms, inclusive, and hydroxy-substituted alkyl having from 1 to 5 carbon atoms, inclusive, and which is otherwise unsubstituted; R‴ is a substituent selected from the group consisting of unsubstituted alkyl having from 1 to 18 carbon atoms, inclusive, hydroxy-substituted alkyl having from 1 to 18 carbon atoms, inclusive, and which is otherwise unsubstituted, unsubstituted alkenyl having from 1 to 18 carbon atoms, inclusive, and phenylalkyl having from 1 to 4 carbon atoms, inclusive, in the alkyl portion thereof; and Y is an acidic anion selected from the group consisting of chloride, bromide, fluoride, iodide, sulfate, sulfonate, phosphate, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate and acetate.

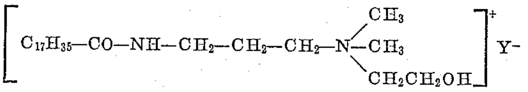
2. The method of promoting crystal growth of 2-aminopyrimidine bisulfite obtained by acidifying with a mineral acid a mother liquor containing in aqueous solution 2-aminopyrimidine and ammonium sulfite, said method comprising adding to the said mother liquor prior to acidification thereof at least about 0.1% of the dry weight of the aforesaid 2-aminopyrimidine bisulfite of a crystal-growth promoter comprising a quaternary ammonium compound of the formula



$$\left[\mathrm{R{-}CO{-}NH{-}CH_2{-}CH_2{-}CH_2{-}}\overset{R'}{\underset{R'''}{\mathrm{N}}}\mathrm{{-}R''}\right]^{+}Y^{-}$$

wherein R is a substituent selected from the group consisting of abietyl and aliphatic hydrocarbon having from 7 to 18 carbon atoms, inclusive, and wherein any unsaturation between adjacent carbon atoms is a double bond; R′ and R″ each is a substituent selected from the group consisting of unsubstituted alkyl having from 1 to 5 carbon atoms, inclusive, and hydroxy-substituted alkyl having from 1 to 5 carbon atoms, inclusive, and which is otherwise unsubstituted; R‴ is a substitutent selected from the group consisting of unsubstituted alkyl having from 1 to 18 carbon atoms, inclusive, hydroxy-substituted alkyl having from 1 to 18 carbon atoms, inclusive, and which is otherwise unsubstituted, unsubstituted alkenyl having from 1 to 18 carbon atoms, inclusive, and phenylalkyl having from 1 to 4 carbon atoms, inclusive, in the alkyl portion thereof; and Y is an acidic anion selected from the group consisting of chloride, bromide, fluoride, iodide, sulfate, sulfonate, phosphate, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate and acetate.

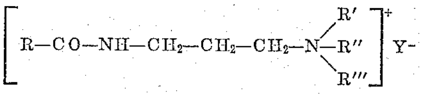
3. The method as in claim 1 wherein the quaternary ammonium compound is the compound of the formula



$$\left[C_{17}H_{35}-CO-NH-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_2CH_2OH}{N}}-CH_3 \right]^+ Y^-$$

wherein Y is an acidic anion selected from the group consisting of chloride, bromide, fluoride, iodide, sulfate, sulfonate, phosphate, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate and acetate.

4. The method which comprises adding to a solution containing a crystallizable organic material selected from the group consisting of 2-aminopyrimidine bisulfite, ferrous calcium citrate and acetylsulfanilyl chloride at least about 0.1% by weight, based on the dry weight of the said crystallizable organic material, of a quaternary ammonium compound of the formula



$$\left[R-CO-NH-CH_2-CH_2-CH_2-\overset{R'}{\underset{R'''}{N}}-R'' \right]^+ Y^-$$

wherein R is a substituent selected from the group consisting of abietyl and aliphatic hydrocarbon having from 7 to 18 carbon atoms, inclusive, and wherein any unsaturation between adjacent carbon atoms is a double bond; R′ and R″ each is a substituent selected from the group consisting of unsubstituted alkyl having from 1 to 5 carbon atoms, inclusive, and hydroxy-substituted alkyl having from 1 to 5 carbon atoms, inclusive, and which is otherwise unsubstituted; R‴ is a substituent selected from the group consisting of unsubstituted alkyl having from 1 to 18 carbon atoms, inclusive, hydroxy-substituted alkyl having from 1 to 18 carbon atoms, inclusive, and which is otherwise unsubstituted, unsubstituted alkenyl having from 1 to 18 carbon atoms, inclusive, and phenylalkyl having from 1 to 4 carbon atoms, inclusive, in the alkyl portion thereof; and Y is an acidic anion selected from the group consisting of chloride, bromide, fluoride, iodide, sulfate, sulfonate, phosphate, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, isocyanate, sulfite, bisulfite, nitrate, nitriate, oxalate, silicate, sulfide, cyanate and acetate, said quaternary ammonium compound promoting the crystal-growth of said crystallizable organic material; crystallizing the said crystallizable organic material from the solution containing both said organic material and said quaternary ammonium compound; and separating the resulting crystalline material from the said solution.

5. A method as in claim 4 wherein the quaternary ammonium compound is a stearamidopropyl dimethyl β-hydroxyethyl ammonium salt of the formula given in claim 17.

6. A method as in claim 5 wherein the stearamidopropyl dimethyl β-hydroxyethyl ammonium salt is stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate.

7. A method as in claim 5 wherein the stearamidopropyl dimethyl β-hydroxyethyl ammonium salt is stearamidopropyl dimethyl β-hydroxyethyl ammonium phosphate.

8. A method as in claim 4 wherein the amount of the quaternary ammonium compound which is added to the solution of the crystallizable organic material is, by weight, from about 0.2% to about 5% of the dry weight of the said crystallizable organic material.

9. A method as in claim 4 wherein the crystallizable organic material is 2-aminopyrimidine bisulfite.

10. A method as in claim 4 wherein the crystallizable organic material is ferrous calcium citrate.

11. A method as in claim 4 wherein the crystallizable organic material is acetylsulfanilyl chloride.

12. In a process of removing by filtration, crystalline particles of 2-aminopyrimidine bisulfite from an aqueous solution containing said particles, said bisulfite being obtained by acidifying with a mineral acid a mother liquor containing in solution 2-aminopyrimidine and ammonium sulfite, the improvement which comprises adding stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate to the said mother liquor prior to acidification thereof, the amount of the said stearamidopropyl dimethyl β-hydroxyethyl ammonium nitrate which is added to the said mother liquor being, by weight, at least 0.1% of the dry weight of the amount of 2-aminopyrimidine bisulfite formed upon acidification of the aforesaid mother liquor containing 2-aminopyrimidine and ammonium sulfite.

13. In a process of removing by filtration crystalline particles of 2-aminopyrimidine bisulfite from an aqueous solution containing said particles, said bisulfite being obtained by acidifying with a mineral acid a mother liquor containing in solution 2-aminopyrimidine and ammonium sulfite, the improvement which comprises adding stearamidopropyl dimethyl β-hydroxyethyl ammonium phosphate to the said mother liquor prior to acidification thereof, the amount of the said stearamidopropyl dimethyl β-hydroxyethyl ammonium phosphate which is added to the said motor liquor being, by weight, at least 0.1% of the dry weight of the amount of 2-aminopyrimidine bisulfite formed upon acidification of the aforesaid mother liquor containing 2-aminopyrimidine and ammonium sulfite.

References Cited by the Examiner

Van Hook, Crystallization: Theory and Practice (New York, 1961), pages 204–6.

IRVING MARCUS, *Primary Examiner.*

H. J. LIDOFF, D. McCUTCHEN, *Examiners.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,180,870

April 27, 1965

Penn F. Spitzer, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 47, for "3-buteny" read -- 3-butenyl --; column 9, line 59, for "nitriate" read -- nitrite --; column 10, line 8, for the claim reference numeral "17" read -- 3 --.

Signed and sealed this 28th day of September 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents