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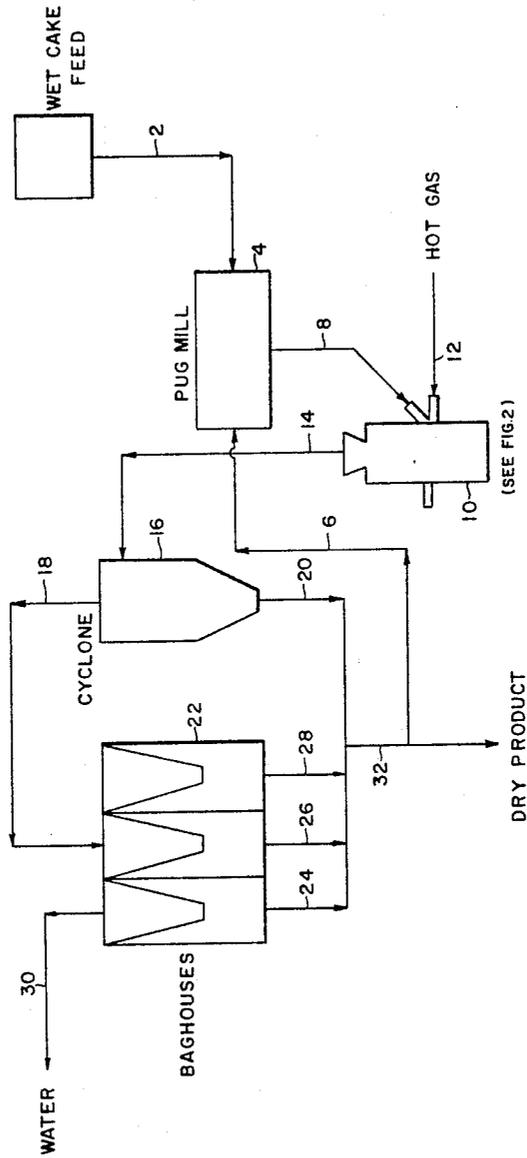
3,289,312

DRYING OF CHLORINATED ISOCYANURATES AND SALTS THEREOF

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2 Sheets-Sheet 1

FIG. 1.



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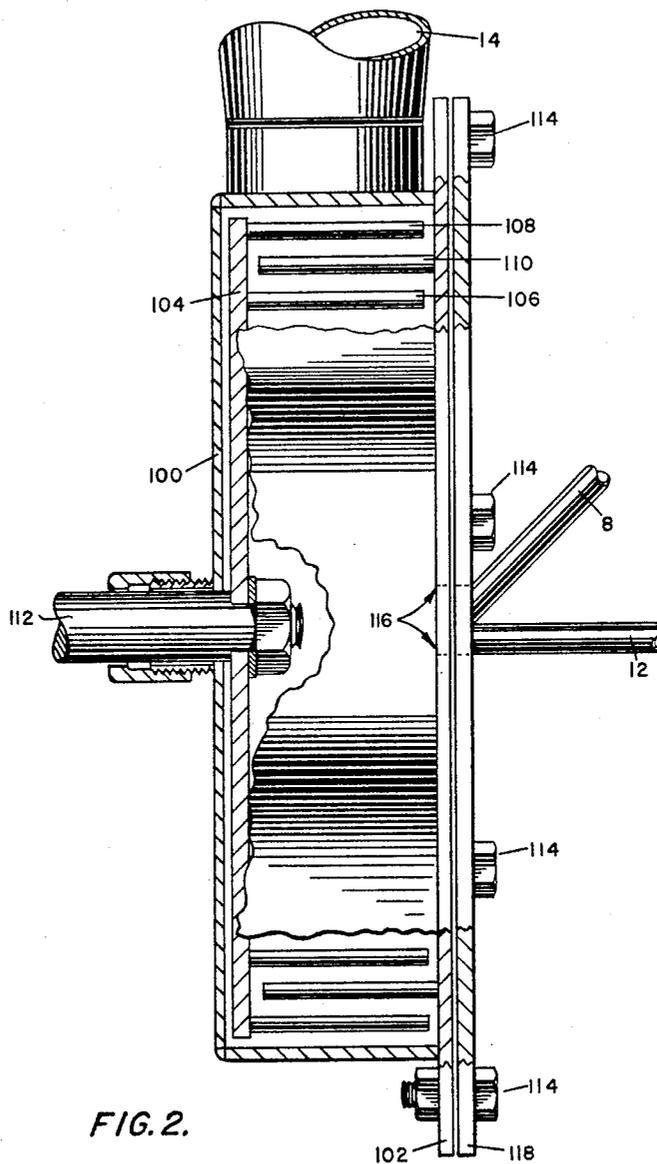
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2 Sheets-Sheet 2



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3,289,312

DRYING OF CHLORINATED ISOCYANURATES AND SALTS THEREOF

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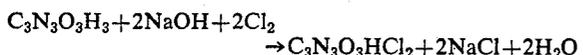
14 Claims. (Cl. 34-10)

This invention relates to an improvement in the production of chlorinated isocyanuric acids and salts thereof, and more particularly, to a rapid method of drying these compounds without the loss of active chlorine.

In this application, the term "chlorinated isocyanuric acids and salts thereof" is intended to cover also chlorinated cyanuric acids and salts thereof, regardless of the tautomeric form in which they may exist.

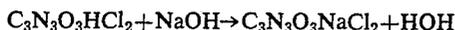
The chlorinated isocyanuric acids and salts thereof have been widely accepted as a source of available chlorine for use in solid bleaching and detergent compositions. The most popular of these compounds are dichloroisocyanuric acid, sodium dichloroisocyanurate, and potassium dichloroisocyanurate. These compounds have found wide acceptance as sources of available chlorine in solid detergent or bleaching compositions because they are relatively stable under ambient conditions and in the absence of substantial amounts of moisture, and are capable of giving off their active chlorine when placed in aqueous solutions intended for bleaching, disinfecting or germicidal action. Trichloroisocyanuric acid, while not as stable as the above salts, nevertheless has been found acceptable in specialty applications where only limited storage is necessary.

Dichloroisocyanuric acid conventionally is prepared by adding elemental chlorine to an alkali metal salt of isocyanuric acid under controlled reaction conditions, as illustrated by the following equation:



Trichloroisocyanuric acid is prepared in the same way except that 3 moles each of the alkali metal hydroxide and chlorine are used per mole of isocyanuric acid.

Sodium dichloroisocyanurate is conventionally prepared by reacting dichloroisocyanuric acid with sodium hydroxide under controlled conditions as illustrated by the following equation:



In similar manner, the potassium salt is produced by using potassium hydroxide in place of sodium hydroxide.

The chlorinated isocyanuric acids and their salts produced by the above processes are dried to their anhydrous state in order to render them acceptable for marketing. The anhydrous form of these acids or salts, containing as little water as possible, is desired because of the increased stability of these compounds in the absence of water and because formulators prefer to use the anhydrous form of these compounds for ease of handling and for incorporation in bleaching and sanitizing formulations.

It has been found most difficult to dry these chlorinated isocyanurates in commercial quantities so that they contain negligible amounts of moisture without reducing their active chlorine contents and without serious loss due to sublimation. The three principal methods that have been employed to dry the chlorinated isocyanuric acids or their salts, either singly or in combination, are

(a) vacuum drying with or without an azeotropic agent at temperatures from 30 to 80° C.

(b) drying in an air-circulating oven at temperatures of up to 110° C., and

(c) spray-drying of an aqueous slurry thereof.

In the vacuum drying technique, the wet, chlorinated isocyanuric acids or their salts are heated to a temperature of from 30 to about 80° C. under vacuum to accelerate drying. This process is effective in removing the water to very low levels without serious degradation of the active chlorine content of these compounds, but it is too slow, requiring many hours of drying.

One improvement on the above technique is set forth in German Patent No. 1,122,535, issued on January 25, 1962, in which a low-boiling organic-water-immiscible solvent is added to the chlorinated cyanuric acid in order to azeotropically remove the water. However, this process is unsatisfactory since it requires handling and maintaining an extraneous organic liquid in the system with the necessary condensing and distilling equipment.

In the second technique, the chlorinated isocyanuric acids or their salts are dried in an oven maintained at 110° C. with mild air circulation through the oven. This technique also is too slow and in addition, results in partial decomposition of the isocyanurates, with release of active chlorine because of the extended time that these compounds are kept in a moist condition at this temperature. The extended drying times are particularly undesirable with respect to the chlorinated isocyanuric acids because these sublime at temperatures above about 100° C. and coat the downstream equipment, including any baghouses, with a film of these acids; the longer the heating is carried out, the more sublimation occurs. This results in premature clogging of the baghouses and in frequent shutdowns to replace them.

In the third method of drying, namely the spray-drying technique, a liquid slurry of the chlorinated isocyanuric acids or their salts is sprayed into a heated gas stream flowing downwardly into a large drying and recovery chamber; the water is flashed off in the drying chamber, leaving a dry residue. This method dries these compounds rapidly but has certain other drawbacks. Chief among these is the fact that relatively large volumes of gases at very high temperatures, i.e. above about 800° F., must be used to dry the chlorinated isocyanurates because of the large amount of water which must be evaporated. The high temperatures result in some decomposition of the product with loss of active chlorine; more serious is the fact that the large volumes of gases required result in sublimation and carry-over of product with subsequent reduction of yield.

In addition, the spray-drier is objectionable because of the lack of uniform drying of different-sized particles. More specifically, after the slurry has been sprayed into the heated gas stream, there is a decreasing temperature gradient over the entire downstream portion of the spray drier during which all of the drying must be effected; the holdup time, and consequently the drying conditions of the particles, vary as they fall through the entire downstream chamber depending upon the size of the particles. The larger, heavier particles that fall more rapidly through the heated gas stream are dried for shorter periods, and at lower temperatures, while the smaller, lighter particles that remain suspended in the gas stream are heated for substantially longer periods and at higher temperatures than the heavier ones. This results in either incomplete drying of the larger particles or some decomposition of the smaller particles with loss of active chlorine. Variations in either the slurry feed rate or the heated gas stream temperature or flow rate aggravate this situation and may result in a product having variable moisture content and variable available chlorine.

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As a result, there is a need for a method of drying the chlorinated isocyanuric acids and their salts to remove substantially all of the moisture, without decreasing their active chlorine content, which is not overly sensitive to process variations, and which produces a uniform, high quality product.

It is an object of the present invention to rapidly dry chlorinated isocyanuric acids and their sodium or potassium salts to a very low moisture content without loss of active chlorine.

It is a further object to obtain as a product a chlorinated isocyanuric acid or salt thereof having a uniformly low moisture content and a uniformly high active chlorine content.

These and other objects will become apparent from the following disclosure.

We have now found a method for rapidly and uniformly drying dichloroisocyanuric acid, trichloroisocyanuric acid, sodium dichloroisocyanurate, potassium dichloroisocyanurate or mixtures thereof to a very low moisture level (on the order of less than about 0.1% moisture) comprising passing a wet cake of the above compounds into a drying zone, finely dividing the cake into discrete particles within the drying zone, passing a gas stream maintained at a temperature of up to about 550° F. through the drying zone at a flow rate of from about 2000 to about 5000 feet per minute, maintaining the temperature of the exit gas from the drying zone at a temperature of from about 220-320° F., maintaining the finely divided discrete particles within the drying zone in contact with the gas stream for a uniform treating time until dry, removing the dried particles from the drying zone in the exit gas stream, and separating these particles of dried compound from the exit gas stream.

In carrying out the present process, the chlorinated isocyanuric acids or their salts are separated from their mother liquors by conventional means, i.e., centrifuges or filters. In the case of the chlorinated isocyanuric acids, any impurities such as sodium chloride, must be washed out of the isocyanurate filter cake before proceeding. The resulting wet cake normally contains from about 5 to about 30% moisture by weight although moisture contents as high as 85% can be handled in this process.

Preferably, the resultant cake is fed by conveyer means into a mixer such as a pug mill. Simultaneously, an anhydrous product stream of the same compound is also fed into the pug mill and mixed with the wet cake. The ratio of the two streams being fed to the pug mill is regulated so that the resultant mixture does not stick or adhere to the inner surfaces of the subsequent drying zone, described below. The sticking of any wet cake in the drying zone must be avoided to prevent prolonged contact with a heated gas stream and subsequent decomposition. In general, the resultant mixture from the pug mill should contain preferably no more than about 5% by weight moisture (total water). Mixtures containing this amount of water have been found to pass through the drying zone without undue sticking. Larger amounts of moisture, over 5%, can be employed, particularly with the chloroisocyanuric acids, as long as no sticking is encountered. For example, the presence of a Teflon or other repellent coatings on the inner surfaces of the drying zone will permit drying of feed streams containing larger quantities of moisture without sticking. In the case of the sodium or potassium dichloroisocyanuric acid salts and dichloroisocyanuric acid, the dry recycle stream can be added in amounts sufficient to theoretically combine with all the free water present so that all of the water is taken up as water of hydration.

The resulting mixture from the pug mill containing preferably no more than about 5% by weight of mois-

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ture is then passed into the drying zone. This zone is made up of a closed chamber containing a cage-type mill and having a feed inlet line, a heated gas stream inlet line, and a gas stream exit line. The cage-type mill, which contains both a rotor and stator section, is rotated at a speed sufficiently high to finely divide the incoming wet cake from the pug mill into discrete particles and maintain them in a fine suspension within the drying zone. Normally, rotation of the cage-type mill rotor at from 500 to 3000 linear feet per minute has been found sufficient to finely divide the wet cake into relatively uniformly sized discrete particles.

Simultaneously, a heated gas stream (normally heated air) is passed through the drying zone at a flow rate of from about 2000 to about 5000 feet per minute. The temperature of the inlet gases is adjusted so that the temperature of the exit gas leaving the drying zone is from about 220-320° F. The salts are preferably dried at exit gas temperatures of from about 260 to about 280° F.; lower temperatures on the order of 230 to 250° F. are preferred for drying the acids to minimize sublimation. The exact temperature of the inlet gas required will depend upon the amount of wet cake that is passed into the drying zone and the moisture content of the wet cake. However, in general, inlet gas temperatures of from about 325 to about 550° F. have been found suitable and result in the desired exit gas temperatures.

In the drying zone, the wet cake is finely divided as it contacts the rotating cage-type mill into relatively uniform particles. These finely divided, suspended discrete particles are then dried by the rapid flow of hot gases through the drying zone. These discrete particles remain in the drying zone for a uniform holdup time regardless of size distribution, until they are substantially dry. The more uniform size distribution of the particles obtained in a cage-type mill aids in obtaining a more uniformly dried product. The dried, discrete particles, which are much lighter than the wet cake fed into the cage-type mill, are carried off in the exit gas stream through the exit gas line located at the top of the drying zone and are then fed to a recovery system for removing the solids from the exit gas stream.

One typical recovery system is carried out by passing the exit gas stream from the drying zone into a cyclone separator to remove the bulk of the separated solids. The effluent gas stream from the cyclone, containing some dried, solid product, is then passed into one or more baghouses for recovery of residual product not separated in the cyclone. The product streams from the cyclone separator and the baghouses are then combined into a single product stream; these solids are in a finely divided state and normally are all -200 mesh with about 50% being -235 mesh. A portion of this product stream can be recycled to the pug mill in order to supply dry recycle for admixture with the wet cake feed.

In the event that the wet cake contains substantially less than about 5% moisture (total water), the use of the pug mill with the dry recycle stream can be eliminated and the wet cake can be fed directly into the drying zone containing the cage-type mill.

After drying has been completed by this process, the resultant anhydrous product normally contains substantially less than about 0.1% by weight total moisture. This moisture level is achieved with little product loss and with virtually no loss of active chlorine during the drying step. This is most important since the loss of even a few percent of active chlorine during the drying stage may render the product unacceptable for commercial marketing. In general, commercial requirements specify a minimum available chlorine level, and if the active chlorine lost during the drying stage reduces the active chlorine level of the resulting product below specifications, the product becomes unacceptable.

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Specific means which may be employed in the practice of this invention are illustrated by way of example in the attached drawings. In the drawings,

FIG. 1 is a schematic representation of an apparatus for carrying out the present invention.

FIG. 2 represents a detailed schematic representation of the evaporator zone represented by 10 in FIG. 1.

In FIG. 1, the wet cake separated from the mother liquor and made up of the chlorinated isocyanuric acids or salts thereof is added to pug mill 4 through conduit 2 where it is mixed with dry, recycled product from conduit 6. The resultant mixture from the pug mill, preferably containing no more than about 5% moisture (total water), is removed from the pug mill through conduit 8 and introduced into drying zone 10. The solids introduced into drying zone 10 are finely divided by means shown in FIG. 2; simultaneously, a heated gas stream is passed into the drying zone through conduit 12. The heated gas stream dries the finely divided solids and these dried solids are carried overhead in the exit gas stream through conduit 14 into cyclone separator 16. The bulk of the solids present in exit gas stream 14 are separated in cyclone 16 and are removed through conduit 20. The remaining gas stream contains a portion of the dried solids which is removed overhead through conduit 18 and introduced into baghouses 22. The remaining finely divided solids in the air stream 18 are separated in baghouses 22 and are removed by conduits 24, 26 and 28. The air stream containing the evaporated moisture is removed via conduit 30. The dried solids recovered from the baghouses and cyclone are combined and recovered as dry products from conduit 32. A portion of the dry product is recycled through conduit 6 to pug mill 4 where it is mixed with the wet cake feed.

Turning now to FIG. 2, a detailed cross-sectional view of evaporator 10 is shown. The drying chamber is made up of an outer container wall 100 to which is attached an annular lip 102. A cover or stator 118 is attached to annular lip 102 by means of bolts 114 to seal the chamber. Adjacent container wall 100 and in space relationship thereto is rotor 104. Two rows of concentric bars 106 and 108 are attached to the rotor 104 and rotate therewith. The rotor is rotated by means of shaft 112 attached to motor means not shown. Attached to the cover (stator) 118 is a single set of bars 110 which project between the concentric circles made up by bars 106 and 108. An opening 116 is present in the center of the cover 118 for entry of both solids and a heated gas through conduits 8 and 12 respectively.

In operation, the rotor 104 with attached bars 106 and 108 is turned by means of shaft 112. Solids are introduced via conduit 8 and opening 116 into the chamber. The gas stream flowing through conduit 12 enters the drying zone 10 through opening 116 and passes through the zone and out through conduit 14. The introduced solids must pass through the maze of rotating bars in order to leave the drying zone through conduit 14. They are finely divided on contact with the bars 106, 108 and 110 by virtue of the small spaced relationship between fixed bars 110 and concentric, rotating bars 106 and 108. In their finely divided state the solids are maintained in a fine suspension within the drying zone by the agitating action of the rotor, and are rapidly dried by the heated gas stream from conduit 12. When the finely divided solids have been dried, the gas stream carries these solids between the rotating bars of the rotor 104 and up through conduit 14 for recovery in downstream equipment.

The following examples are given to illustrate the invention and are not to be deemed limiting thereof.

EXAMPLE 1

One hundred and twenty pounds of a potassium dichloroisocyanurate wet cake, assaying 59.9% available chlorine and containing 16% water, was continuously fed into a pug mill at a rate of 2 lbs./min. for 1 hr. Simul-

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taneously, anhydrous, finely divided potassium dichloroisocyanurate, assaying 59.9% available chlorine, was added to the pug mill at a uniform rate in a weight ratio to the wet cake of 3:1 during the entire 1 hr. addition time. The anhydrous potassium dichloroisocyanurate was supplied to the pug mill first from an outside source and then by recycle of some of the dried product from the process. The resulting mixture from the pug mill was introduced into a drying zone such as described and shown in FIG. 2. Simultaneously, heated air was passed at a rate of 2700 f.p.m. through the drying zone. The inlet temperature of the air was 500° F. The rotor was rotated to drive the cage-type mill at 2000 linear feet per minute. The resulting air stream from the drying zone was passed through a cyclone and baghouse recovery system such as shown in FIG. 1 for recovery of the dried potassium dichloroisocyanurate. The recovery system yielded a total of 124 pounds of potassium dichloroisocyanurate, of which 25 lbs. was initially supplied from an outside source as dry recycle. This amounted to a yield of 98.2% of the wet cake fed into the system. The resultant product had a moisture content of 0.07% and an available chlorine content of 59.9%. A 1% aqueous solution of the product gave a pH of 6.2.

EXAMPLE 2

The procedure recited in Example 1 was repeated except that sodium dichloroisocyanurate was employed in place of the potassium salt. The resultant product had a moisture content of 0.09%, had no measurable loss of available chlorine during the drying operation, and the final product was recovered in greater than 98% yield.

EXAMPLE 3

Eighty pounds of a water-washed wet cake of trichloroisocyanuric acid, assaying 91% available chlorine and containing 5% moisture, was fed directly into an evaporating zone and recovery system as described and illustrated in FIG. 1 and FIG. 2, at a uniform rate over a one hour period. The wet cake was fed directly to the evaporator without being mixed with dry recycle in the pug mill. Air was passed through the evaporating zone at a rate of 2900 f.p.m. The inlet temperature of the gas stream was between 425 and 450° F. and the outlet temperature was maintained at between 250 and 265° F. The rotor was rotated to drive the cage-type mill at 2000 linear feet per minute. At the end of the run, 75 lbs. of -200 mesh trichloroisocyanuric acid, assaying 0.008% water and 90.5% available chlorine, was recovered. The yield was 98.8%.

EXAMPLE 4

The process of Example 3 was repeated except that dichloroisocyanuric acid was used in place of trichloroisocyanuric acid. The resultant product contained 0.01% moisture and the yield was over 98%. No measurable amount of available chlorine was lost during the drying stage.

While the above process is most useful in drying the chlorinated isocyanuric acids and their salts, it can also be used for drying cyanuric acids per se. However, since cyanuric acid is more stable than the chlorinated form thereof or the chlorinated salts thereof, higher temperatures can be employed. For example, input gas temperatures to the evaporating zone of from 600 to about 800° F. can be used; outlet temperatures from about 230 to 400° F. can be used with about 300 to 320° F. being preferred.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims,

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the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A method for rapidly drying a labile compound selected from the group consisting of dichloroisocyanuric acid, trichloroisocyanuric acid, sodium dichloroisocyanurate, and potassium dichloroisocyanurate, comprising passing a wet cake of said compound into a drying zone, finely dividing and beating said cake into discrete particles by beater means, passing a gas stream maintained at a temperature up to about 550° F. through said drying zone at a flow rate of from about 2000 to about 5000 feet per minute, maintaining the temperature of the exit gas from said drying zone at a temperature of from about 220 to about 320° F., maintaining said discrete particles within said drying zone in contact with said gas stream for a uniform treating time until dry, removing particles of dry compound from said drying zone in the exit gas stream, and separating said particles of dry compound from said exit gas stream.

2. Process of claim 1 in which said wet cake of said compound contains from about 5 to about 30% moisture.

3. Process of claim 1 in which the dry compound contains no more than about 0.1% by weight residual moisture.

4. Process of claim 1 in which the compound is dichloroisocyanuric acid.

5. Process of claim 1 in which the compound is trichloroisocyanuric acid.

6. Process of claim 1 in which said compound is sodium dichloroisocyanurate.

7. Process of claim 1 in which said compound is potassium dichloroisocyanurate.

8. A method for rapidly drying a labile compound selected from the group consisting of dichloroisocyanuric acid, trichloroisocyanuric acid, sodium dichloroisocyanurate and potassium dichloroisocyanurate, comprising mixing a wet cake of said compound with sufficient quantities of anhydrous compound so that the resulting

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mixture has a moisture content of no more than about 5% by weight, passing said mixture into a drying zone, finely dividing and beating said mixture into discrete particles by beater means within said drying zone, passing a gas stream maintained at a temperature up to about 550° F. through said drying zone at a flow rate of from about 2000 to about 5000 feet per minute, maintaining the temperature of the exit gas from said drying zone at a temperature of from about 220 to about 320° F., maintaining said discrete particles within said drying zone in contact with said gas stream for a uniform treating time until dry, removing particles of dry compound from said drying zone in the exit gas stream, and separating said particles of dry compound from said exit gas stream.

9. Process of claim 8 in which said wet cake of said compound contains from about 5 to about 30% moisture.

10. Process of claim 8 in which the dry compound contains no more than about 0.1% by weight residual moisture.

11. Process of claim 8 in which the compound is dichloroisocyanuric acid.

12. Process of claim 8 in which the compound is trichloroisocyanuric acid.

13. Process of claim 8 in which said compound is sodium dichloroisocyanurate.

14. Process of claim 8 in which said compound is potassium dichloroisocyanurate.

References Cited by the Examiner

UNITED STATES PATENTS

2,115,645	4/1938	Pehrson et al.	34—57
2,290,068	7/1942	Petersen	34—10 X
2,350,162	5/1944	Gordon	34—10
2,657,797	11/1953	Ledgett et al.	34—10 X
2,975,142	3/1961	Schmidt et al.	252—99 X
3,112,274	11/1963	Morgenthaler et al.	252—99

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