

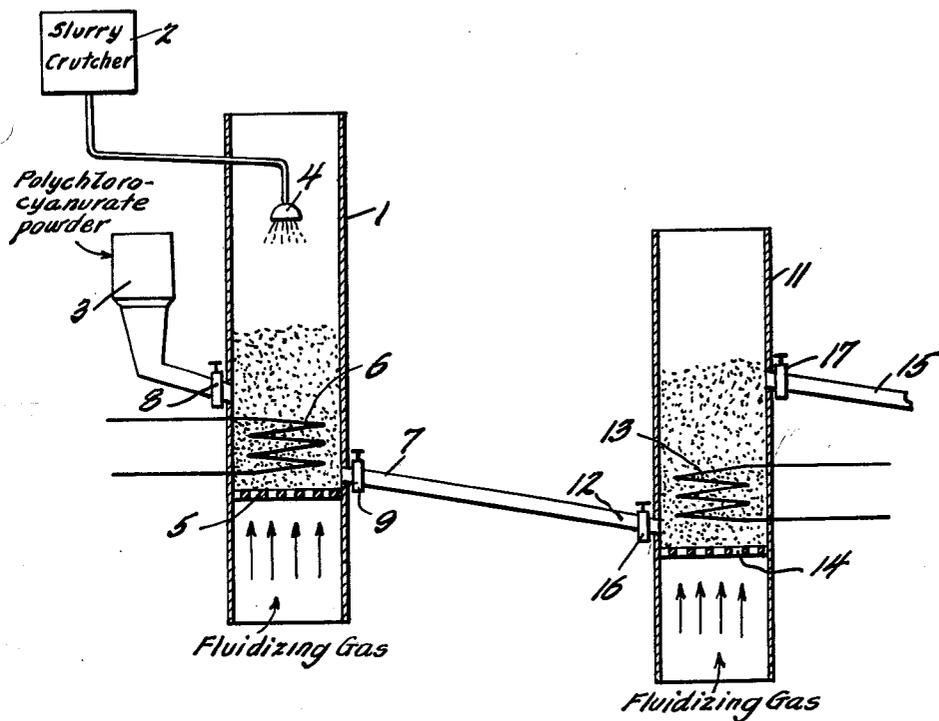
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PROCESS FOR MAKING A BLEACH COMPOSITION

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3,112,274

**PROCESS FOR MAKING A BLEACH COMPOSITION**  
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This invention relates to a process for making a dry bleach composition. More particularly, it is a process for coating a chlorinated organic bleaching compound with inorganic salts in a fluidized bed in order to obtain a dry bleach composition having outstanding characteristics.

Dry chlorine bleach compositions have advantages over the widely used liquid hypochlorite solution which include ease in packaging, handling and shipping. Moreover, dry chlorine bleach compositions can be combined advantageously with dry products such as granular detergents whereas liquid bleaches cannot.

The polychlorocyanurates, i.e. tri- and di-chloro cyanuric acids and the alkali metal salts of dichlorocyanuric acid, have found wide acceptance as stable and efficient dry organic bleaching compounds. The polychlorocyanurates are usually mixed with dry inorganic salts, preferably alkaline salts, as carrier agents to provide bulk for ease in measuring and for prevention of localized over-concentration and preferably to provide alkalinity when the bleaching compound is dissolved in water. It has been found that polychlorocyanurates provide the greatest bleaching activity in water under alkaline conditions.

Mechanical mixtures of polychlorocyanurates and inorganic carrier agents are not satisfactory because of a definite tendency for stratification to occur in the packaged dry composition when it is moved or shipped because of the inherent difference in particle size and density of the polychlorocyanurates and the carrier agents. Commercially available polychlorocyanurates are usually fine dusty particles. Stratification of the polychlorocyanurate and the carrier agent is very undesirable, since users are unable to obtain uniform results with portions of the composition taken from different parts of the package.

In order to produce a dry substantially homogeneous mixture of a polychlorocyanurate and an inorganic carrier agent that will not stratify when packaged, aqueous slurries of the polychlorocyanurate and the carrier agent have been dried, usually by spray drying. Forming and drying such aqueous slurries, particularly spray drying, have caused substantial difficulties.

When polychlorocyanurates are incorporated in aqueous slurries preparatory to drying, there is a loss of available chlorine because of hydrolysis, thus undesirably reducing the effectiveness of the compounds. The elevated temperatures then used to eliminate the water from such slurries, particularly those temperatures used in spray drying, cause additional loss of available chlorine. Spray drying of slurries containing polychlorocyanurates is also complicated by the corrosive action of the polychlorocyanurates on the crutchers, spray nozzles and spray towers.

The polychlorocyanurate in dry bleach compositions dried in accordance with the usual methods, such as by spray drying, are not protected or are only partially protected from moisture and air which are known to increase the tendency of such compounds to decompose. For example, the process of spray drying a homogeneous aqueous slurry of a polychlorocyanurate and an inorganic carrier agent effects a combination of the two ingredients in a granule which is usually hollow. Polychlorocyanurate in a spray dried granule will be exposed on the entire surface of the granule. Only the polychlorocyanurate in the interior of the granule will be protected by the carrier agent. Thus, the exposed polychlorocyanurate is subject

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to attack not only from moisture and air but from reactive materials with which the chlorine compound may be contacted such as strongly alkaline materials, organic foaming agents, optical brighteners and the like. Exposed polychlorocyanurate also provides a distinct chlorine odor to which some people might object and which would interfere with desired perfuming. The use of organic coating materials such as waxes, soaps, paraffins, fatty alcohols and the like is undesirable because of the reactivity of such materials with the polychlorocyanurates, because coating with such materials is difficult, and because such materials tend to leave a residue in the water in which the polychlorocyanurate is used.

It is an object of this invention to provide a process for making homogeneous dry bleach compositions containing a polychlorocyanurate and an inorganic carrier agent which does not result in undue loss of available chlorine.

It is another object of this invention to provide a process for making a homogeneous, dry bleach composition comprising a polychlorocyanurate having an inorganic coating which protects the polychlorocyanurate from attack from moisture, air, and reactive organic materials.

It is a further object of this invention to provide a process for making a homogeneous, dry bleach composition which is stable and the ingredients of which do not tend to stratify or segregate when packaged.

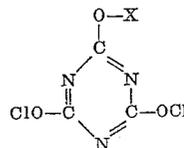
It is a further object of this invention to provide a dry bleach composition containing a polychlorocyanurate which has little or no chlorine odor.

Speaking broadly, it was found that these and other objects can be attained by suspending dry particles of a polychlorocyanurate in an upward flowing gaseous current to form a fluidized bed, and spraying onto this bed an aqueous slurry of an inorganic salt, preferably an alkaline salt, whereby a coating is formed around the polychlorocyanurate particles which is then dried. The resulting product is a stable, effective dry bleaching composition comprising a core of the polychlorocyanurate coated with an inorganic material which protects the chlorine compound from attack from air, moisture and reactive organic materials. The process, as more specifically hereinafter described, involves low temperature and low moisture conditions relative to the usual drying processes, such as spray drying, thereby markedly reducing the loss of available chlorine during the processing of the polychlorocyanurates. The process involves a lesser amount of equipment which is subject to corrosive attack than spray-drying processes.

It is to be pointed out that this invention is not merely the application of the fluidized bed technique to coat and protect particles of chlorine compounds. The problems involved in working with the specific materials employed and the solutions to these problems, as more fully hereinafter described, constitute the essence of the invention.

The description of the process employed and the dry bleach composition produced thereby which is herein-after more fully set forth, will be more clearly understood when taken in conjunction with the drawing which shows a flow diagram.

Polychlorocyanurates have the formula



wherein X is Cl (trichlorocyanuric acid), H (dichlorocyanuric acid), or an alkali metal such as Na (sodium dichlorocyanurate) or K (potassium dichlorocyanurate). Tautomeric forms of polychlorocyanurates and methods

for making polychlorocyanurates are discussed in U.S. Patents 2,607,738 and 2,913,460. The preferred polychlorocyanurates are sodium and potassium dichlorocyanurates since they are more stable than the polychlorocyanuric acids.

The inorganic material which is used to coat the polychlorocyanurate particles in the fluidized bed comprises aqueous slurries of inorganic salts which are dried to form a protective film around the particles. Examples of such inorganic salts are sodium and potassium sulfates, phosphates, carbonates and borates. Slurries of such salts should have a pH in the range of about 4 to about 11. A slurry having a pH higher than about 11 undesirably decreases the stability of the polychlorocyanurate particles on which it is sprayed. The halides and ammonium compounds are not suitable since they tend to cause decomposition or degradation of the polychlorocyanurates. Sodium tripolyphosphate and mixtures of sodium tripolyphosphate and sodium sulfate wherein the amount of sodium sulfate is up to three times the amount of sodium tripolyphosphate are extremely useful in the process of this invention since they provide a good coating and the desired buffered alkalinity for the optimum bleaching activity of the polychlorocyanurate. Other examples of inorganic salts useful in the process of this invention are sodium carbonate, sodium tetraborate, potassium sulfate, sodium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium orthophosphate (mono- and di-basic) and potassium bicarbonate.

Minor amounts of anionic organic detergents can advantageously be included in the slurries of coating material to increase the agglomeration tendencies of the coated particles. Agglomeration is hereafter more fully described. Such detergents are soap and non-soap synthetic detergents of the sulfuric and sulfonic ester type which also contain in their molecular structure an alkyl or acyl radical containing from 8 to 18 carbon atoms. However, such detergents should not contain amine or amide groups because of the reactivity of the nitrogen in these groups with the polychlorocyanurates. For example, amine soaps and acyl taurides are undesirably reactive with the polychlorocyanurates. Non-ionic detergents, such as higher fatty acid mono- and di-ethanol amides, are also undesirable.

The following soaps are examples of useful additions to the slurry of coating material used in the process of this invention: sodium and potassium salts of the higher fatty acids of naturally occurring plant or animal fats and oils (e.g. palm oil, coconut oil, soybean oil, castor oil, tall oil, tallow, whale and fish oils, grease and lard) or of synthetically produced fatty acids. Sodium and potassium soaps can be made by direct saponification of the fats and oils or the neutralization of the free fatty acids.

The following water-soluble, anionic, organic, non-soap, synthetic detergents are examples of useful additions to the slurry of coating material used in the process of this invention: sodium and potassium alkyl glyceryl ether sulfonates, especially those ethers of higher fatty alcohols derived by the reduction of coconut oil; the reaction product of higher fatty acids with sodium or potassium isethionate, where, for example, the fatty acids are derived from coconut oil; sodium or potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms in either a straight chain or preferably a branched chain which is derived from polymers of propylene; dialkyl esters of sodium or potassium salts of sulfosuccinic acid, for example the dihexyl ester; sodium and potassium alkyl sulfonates and sulfates, especially those alkyl sulfates derived by sulfation of higher fatty alcohols produced by reduction of tallow or oils of the coconut oil group, such as coconut and palm kernel oils; sodium and potassium salts of sulfated or sulfonated monoglycerides derived, for example, from coconut oil; sodium or potassium salts of the

higher fatty alcohol esters of sulfocarboxylic acids, for example, the sodium salt of the lauryl alcohol ester of sulfoacetic acid. Sodium alkyl sulfate is the preferred anionic detergent because of its extremely low tendency to react with the polychlorocyanurates.

Fluidization is a technique widely used in catalytic cracking. Fluidization involves the formation of a bed of a dense phase of finely divided solids suspended in an up flowing gaseous stream under such conditions that the solids are in turbulent, random motion within the bed, while the bed maintains an upper free surface resembling that of boiling liquid. The vessel in which a fluidized bed is maintained has provision at the bottom for providing the even distribution of the up-flowing gas over the cross section of the vessel such as the use of a porous plate. The velocity of the gas is sufficiently high to buoy the finely divided solids in a turbulent, fluid-like motion. The gas velocity must be sufficient to buoy the solids in this manner but must not be so great that the bed will be swept out of the container or that the bed will lose its upper free surface. The variables of fluidized beds, i.e. kinetics, particle size, gas velocity, apparatus, etc., have been extensively studied and reported. See, for example, "Fluidization" edited by D. F. Othmer (Reinhold, 1956) and "Fluidization" by Max Leva (McGraw-Hill, 1959).

In the process of this invention the slurry of inorganic coating material is sprayed onto the particles of polychlorocyanurate in the fluidized bed. This method of spray coating has advantages over other methods in which the particles to be sprayed are in a falling stream, a tumbling drum or on a screen. In the fluidized bed, a very large amount of particle surface is exposed and the drying efficiency of the fluidizing gas and the coating completeness are very great. In a fluidized bed the treated particles are easily removed and transported since the fluidized solids behave similar to a liquid.

It was found that the effective utilization of a fluidized bed and spray-coating of the inorganic material to accomplish the objects of this invention require specific and carefully controlled steps and conditions. It was found that the conditions necessary for satisfactory spray-coating of the polychlorocyanurate particles in the fluidized bed are not suitable for the effective drying of the coated particles to a finished useful dry bleach product. Conversely the conditions required for effective drying are not suitable for the coating operation. The requirements of the coating and drying steps are more fully hereinafter described.

Thus, the process of this invention in more specific terms involves forming a fluidized bed consisting of a dense phase bounded by an upper free surface by passing a distributed ascending current of gas at a predetermined velocity through a mass of solid particles of a polychlorocyanurate, heating the bed to a temperature in the range of about 100° F. to about 170° F. and spraying onto the particles in the thus formed bed an aqueous slurry of an inorganic coating material selected from the group consisting of sodium and potassium sulfates, phosphates, borates and carbonates to coat the particles in the bed. Sufficient coating is sprayed on the particles to obtain coated particles having a weight ratio on an anhydrous basis of polychlorocyanurate to coating material in the range of about 3:1 to about 1:5. The bed is maintained in the temperature range of about 100° F. to about 170° F. until the free moisture content of the coated particles is in the range of about 1% to about 15%. The coated particles are then dried at a temperature in the range of about 190° F. to about 240° F. to a free moisture content of 0% to about 2%. The final drying step can be effected in the same vessel as the earlier steps by increasing the temperature of the fluidized bed. Drying can also be effected by fluidizing the partially dried coated particles in a second fluidized bed, by tumble drying them

in a rotary drum drier, or by drying the particles on a moving belt in an oven.

The process can be made continuous by continuously supplying the fluidized bed with uncoated polychlorocyanurate powder, continuously spraying on the slurry of inorganic coating material and continuously drawing off partially dried coated particles which are then dried continuously, preferably in fluidized bed in a second fluidizing vessel, where finished dried product is continuously drawn off.

As used in connection with the description and claims of the present invention the expression "free moisture" means moisture other than that of the water of hydration existing in inorganic salt hydrates which are stable (retain their water of hydration) at least up to 120° F. For example, the water in sodium sulfate decahydrate is classed herein as free moisture because sodium sulfate decahydrate is stable only up to about 90° F. where its water of hydration is liberated. However, the water in sodium tripolyphosphate hexahydrate is not classed as free moisture because that hydrated salt is stable up to about 220° F.

The preferred practice of the invention will now be described in more detail and with specific reference to the flow diagram of the accompanying drawing.

The polychlorocyanurate powder is introduced from its storage 3 into the fluidizing vessel 1 in a quantity predetermined to form a fluidized bed of the desired size. Valve 8 is then closed. The powder is then formed into a fluidized bed by forcing a gas which is substantially inert to the powder such as air or nitrogen, through the grid 5.

The grid 5 is preferably a porous plate but any grid can be used which provides substantially even distribution of the upward flowing gas over the cross section of the fluidizing vessel 1.

If a porous plate is used, it should be porous enough to permit upward passage of air without an unduly large pressure drop but should not be so porous that substantially even distribution of the fluidizing gas is not obtained. The porous plate can be made of sintered stainless steel or of a porous ceramic material. Instead of porous plates, finely perforated plates, fine screens or bubble cap plates of the type used in distilling and deodorizing columns can be used as grids. A grid can be dispensed with in smaller fluidizing vessels which have a conical bottom which evenly distributes the fluidizing gas.

The velocity of the fluidizing gas should be sufficient to buoy the polychlorocyanurate particles into a fluidized bed but should not be so great that the upper free surface of the bed is lost either by extreme bubble formation or slugging within the bed (severe vertical surging of the bed) or by sweeping the particles out of the vessel. Polychlorocyanurate powders having a particle size in the range of about 5 $\mu$  to about 5 mm., preferably 20 $\mu$  to 850 $\mu$ , can be formed into the fluidized beds which are useful in the process of this invention. Particles smaller in size than about 5 $\mu$  are too fine to form properly into a bed. It has been found that gas velocities in the range of about 1 ft./sec. to about 10 ft./sec., preferably 2 ft./sec. to 6 ft./sec., should be used with polychlorocyanurate powders in the above particle size range to form satisfactory fluidized beds. These velocities and the velocities hereinafter mentioned are measured after the fluidizing air has risen above the upper free surface of the bed and are more useful figures than velocities measured below or within the bed.

The height of the fluidized bed does not appear to be a critical factor in the practice of this invention; however, the best fluidization and processing results occur when the bed height is between 1 and 2 feet. Practical fluidizing vessel diameters range from about 1 to about 5 feet. Bed heights higher than 2 feet can be used in vessels having a diameter of about 3 to 5 feet.

The temperature within the fluidized bed should be

maintained in the range of about 100° F. to about 170° F. To maintain a temperature within this range the fluidizing gas can be heated or a heating coil 6 or heated rods can be placed in the bed or a heating jacket can be placed around the portion of the fluidizing vessel within which the bed is located. Preferably, the bed temperature is maintained partially with heated fluidizing air and partially with a heating means in or around the bed. Heating of the bed is easier to control if both methods of heating are used since each method uses a lower temperature than if only one method were used.

After the bed has been formed and it is at the desired temperature, the slurry of coating material from crutcher 2 is sprayed on to the bed through spray nozzle 4 from a point above the upper free surface of the bed. The spray nozzle 4 is a conventional atomizing nozzle using pressure atomization or preferably a two fluid nozzle using air or other inert gas as the atomizing fluid. Liquid spray pressures can be in the range of about 10 p.s.i. to about 100 p.s.i. with air or gas pressures in the range of about 10 p.s.i. to about 100 p.s.i.

The slurry of coating material should have a water content in the range of about 30% to about 85%. Less than about 30% water results in a viscous slurry which is hard to spray, increases the tendency of the slurry to spray dry and makes difficult the coating of the polychlorocyanurate powder. More than about 85% water in the slurry results in poor coating characteristics and a high evaporative load in the process. The preferred range is 55% to 75%.

The slurry temperature should be high enough to obtain a pumpable viscosity but not be so high that there is undesirable spray drying on atomization. Satisfactory slurry temperatures vary with slurry composition but the preferred temperatures for slurries containing sodium tripolyphosphate and/or sodium sulfate are in the range of about 70° F. to about 140° F.

As mentioned above, the temperature maintained within the bed during the coating step is in the range of about 100° F. to about 170° F. A temperature within this range coupled with the evaporative effect of the fluidizing gas results in the formation of the inorganic coating around the polychlorocyanurate particles and in the partial drying of this coating. The temperature should not be less than about 100° F. in order to prevent the build-up of so much water in the coated particles that proper fluidization is prevented. If the temperature exceeds about 170° F. the atomized slurry of coating material has a tendency to be spray dried, which prevents effective coating of the polychlorocyanurate particles. The preferred temperature range is 120° F. to 150° F.

Sufficient coating material should be sprayed on the polychlorocyanurate particles to obtain a weight ratio of coating material to polychlorocyanurate in the finished product in the range of about 1:3 to about 5:1, preferably 1:1.5 to 2:1, on an anhydrous basis.

The tendency of the coated particles to agglomerate with each other in the form of clumps of coated particles (if it is desired to have a larger particle size in the finished product) can be increased by adding a small amount of an anionic organic detergent to the slurry of coating material. The detergent imparts a stickiness to the coated particles causing increased agglomeration. The slurry can contain from 0% to about 1.5% anionic detergent for agglomeration purposes with the size of the agglomerate increasing with increasing amounts of detergent. Amounts greater than about 1.5% result in an undesirably large increase in the size of the agglomerates making the operation of the fluidized bed difficult. 0.5% to 1% is the preferred amount of detergent in the slurry. The amounts of anionic detergent present in the slurry necessarily determine the amounts of anionic detergent present in the coating (on an anhydrous basis) since the range of water content in the slurry has hereinbefore been given. Since the solids in the slurry provide the coating

for the polychlorocyanurate particles, a simple ratio balance will give the percentage range of anionic detergent in the coating. Thus, the coating comprises, on an anhydrous basis, 0% to about 10% anionic detergent, preferably 0.7% to 6.7%.

The fluidized bed is maintained in the above temperature range until the free moisture content of the coated particles is in the range of about 1% to about 15%. To attempt to dry the coated particles to a free moisture content of less than about 1% at a temperature of not more than about 170° F. would result in a long and inefficient process. The length of time that would be required would result in an undesirable loss of chlorine. Therefore, after the particles have been coated and the possibility of spray drying the atomized slurry of coating material is passed, and flow of coating spray has been discontinued, efficient drying of the coated particles can be effected by subjecting the coated particles to a temperature in the range of about 190° F. to about 240° F. Efficient drying is difficult to obtain at a temperature less than about 190° F. At temperatures exceeding about 240° F. there is a tendency for decomposition of the polychlorocyanurate. The preferred temperature range is 205° F. to 235° F. The coated particles are dried in this step to a free moisture content in the range of 0% to about 2%. The finished product should not contain more than about 2% free moisture, preferably not more than about 1%, since more than this amount decreases the stability of the product and makes the product sticky with a tendency to cake. The preferred free moisture content of the final product is 0%. If a hydrated inorganic salt which is stable up to at least about 120° F. is used as a coating material, it is desirable to drive off a portion of the water of hydration during the drying step to a point where the final product contains as low as about 2% total water. This permits the final product to take up some moisture from the atmosphere, if it is so exposed, without the water so taken up becoming free moisture.

The final drying step can be effected in several ways depending on the type of operation desired. In the batch process the coated particles can be retained in fluidizing vessel 1 while the bed temperature is increased from a temperature in the range of about 100° F. to about 170° F. to a temperature in the drying range of about 190° F. to about 240° F. When the desired moisture content is reached valve 9 is opened and the finished product is discharged through discharge 7. If it is not desired to change the temperature in fluidizing vessel 1, the partially dried coated particles can be run through valve 9, discharge 7, inlet 12 and valve 16 into another fluidizing vessel 11. In this second fluidizing vessel 11, the partially dried coated particles are formed into a fluidized bed in the same manner that a bed is formed in the first fluidizing vessel 1. The bed is maintained at a temperature in the range of about 190° F. to about 240° F. with either heated fluidizing gas passing through grid 14 or a heating coil 13 or jacket or, as explained above, preferably both. A temperature in this range is maintained until the coated particles are dried to a free moisture content in the range of 0% to about 2% at which time valve 17 is opened and the finished product is discharged through discharge 15.

The final drying can be effected by drying means other than a second fluidized bed such as by tumble drying in a low speed rotary drum drier or by drying on a moving belt in an oven. Drying in a fluidized bed is preferred because it is efficient, it is an enclosed system and the fluidizing air facilitates removal of fines.

In a continuous process the processing conditions are about the same as those described above when two fluidizing vessels are used. However, in a continuous process, valves 8, 9, 16, and 17 are left open and there is a continuous input of polychlorocyanurate powder from its source 3 to maintain the bed, continuous spray-on from spray nozzle 4, continuous discharge of coated, partially dried particles from discharge 7, continuous input

of these particles through inlet 12, continuous drying of these particles in fluidizing vessel 11 and continuous discharge of the finished dried particles through discharge 15. Preferably valve 8 is below the upper free surface of the bed. An efficient continuous process is possible because in fluidizing vessel 1, the coated particles, being heavier than the uncoated polychlorocyanurate powder, will migrate to the lower portion of the fluidized bed where they can be drawn off through discharge 7. Thus, valve 9 is preferably located at the lowest portion of the fluidized bed in the coating operation to minimize the proportion of uncoated or partially coated particles drawn off. Then in fluidizing vessel 11, the dried coated particles, being lighter than the partially dried coated particles entering in the lower portion of the fluidized bed, will migrate to the upper portion of the fluidized bed where they can be drawn off through valve 17 and discharge 15.

A continuous process can also be obtained if the final drying step is performed by drying means other than a second fluidized bed such as by continuous passage through a rotary drum drier or an oven.

The following examples are given to illustrate the manner in which this invention can be practiced. All percentages are by weight.

Example I

A slurry consisting of 35% sodium tripolyphosphate and 65% water was added to a crutcher and heated to 92° F.

10 pounds of sodium dichlorocyanurate powder was added to a circular fluidizing vessel which had a diameter of 12 inches. The powder had a particle size corresponding to the following sieve analysis (Tyler standard sieve):

	Percent
On 65 mesh.....	14
Through 65 mesh, on 150 mesh.....	11
Through 150 mesh, on 325 mesh.....	24
Through 325 mesh.....	51

The vessel had a grid which consisted of a plate of sintered powdered stainless steel. The plate was 1/16 inch thick and had a porosity grade of "D" as described in an article by J. E. Campbell on pages 98-101 of *Materials and Methods*, April 1955. The powder was formed into a fluidized bed by passing air, evenly distributed by the grid over the cross-section of the vessel, at 168° F. upward through the grid. The velocity of the air as measured above the bed was 2.27 feet per second. The air had sufficient velocity to buoy all of the particles of powder in a fluidized bed having an upper free surface. Heating coils located within the bed area of the vessel were heated to 368° F. with steam.

The slurry was sprayed downward onto the bed through a two-fluid spray nozzle located 24 inches above the upper free surface of the bed. Air at 50 p.s.i. was the atomizing fluid and the slurry was pumped through the nozzle at 27 p.s.i. The bed temperature was 125° F.

The slurry was sprayed onto the bed until a coating of sodium tripolyphosphate had formed around the sodium dichlorocyanurate particles in the weight ratio, on an anhydrous basis, of coating to sodium dichlorocyanurate of 1.2:1. The coated particles had a free moisture content of 1.4%.

The coated particles were then dried by increasing the bed temperature to 205° F. The heating coil temperature was 368° F. and the fluidizing air temperature was 171° F. The drying was stopped when the free moisture of the coated particles was completely eliminated.

The final product had the following composition:

	Percent
Sodium tripolyphosphate.....	47.1
Sodium dichlorocyanurate.....	39.1
Water (as hydrate).....	13.8

This product was a stable granular dry bleach com-

position which when dissolved in water provided active and efficient bleaching, sterilizing and disinfecting properties. The sodium tripolyphosphate provided the solution with the desired buffered alkalinity and sequestered water hardness ions. The coating of sodium tripolyphosphate around the sodium dichlorocyanurate salt particles provided greater storage stability and resistance to attack from air or moisture than either the untreated salt or the salt spray dried with an equivalent amount of sodium tripolyphosphate. The granules had only a very slight chlorine odor. The granules were substantially uniform in composition throughout the product and there was no noticeable tendency for the ingredients of the composition to segregate.

A mixture of equal parts by weight of sodium tripolyphosphate and sodium sulfate can be substituted for the sodium tripolyphosphate in an equal amount by weight in Example I with substantially the same results.

#### Example II

A slurry consisting of 34.2% sodium sulfate, 0.7% sodium coconut oil alcohol sulfate and 65.1% water was added to a crutcher and heated to 100° F.

10 pounds of the sodium dichlorocyanurate described in Example I were added to the fluidizing vessel and formed into a fluidized bed as described in Example I except that the air temperature was 178° F. and the heating coil temperature was 370° F.

The slurry was sprayed on to the bed as described in Example I except that the air was at 50 p.s.i. and the slurry pressure was 18 p.s.i. The bed temperature was 116° F. Spraying continued until a sodium sulfate coating had formed around the sodium dichlorocyanurate in a ratio of coating to sodium dichlorocyanurate of 1:1.1 on an anhydrous basis. The coated particles had a free moisture content of 12.4%.

The coated particles were then dried by increasing the bed temperature to 235° F. The heating coil temperature was 370° F. and the fluidizing air temperature was 178° F. The drying was stopped when the free moisture content of the coated particles was 0.7%.

The final product had the following composition:

	Percent
Sodium sulfate.....	46.3
Sodium coconut alkyl sulfate.....	1.0
Sodium dichlorocyanurate.....	52.0
Water .....	0.7

The final product was an outstanding granular dry bleach composition having characteristics substantially the same as the product described in Example I except that the sodium sulfate provided no buffered alkalinity or sequestration in solution.

In Example II, potassium tripolyphosphate, tetrasodium pyrophosphate, sodium tetraborate or potassium bicarbonate can be substituted in equal amounts by weight for the sodium sulfate with substantially equal results. These compounds provide alkaline solutions and/or sequestering properties.

#### Example III

A slurry consisting of 34.43% sodium tripolyphosphate, 0.35% sodium coconut oil alcohol sulfate, 0.22% ultramarine blue (for coloring purposes) and 65% water was added to a crutcher and heated to 90° F.

20 pounds of the sodium dichlorocyanurate powder having the particle size described in Example I was added to a circular fluidizing vessel having the diameter and grid characteristics described in Example I. The powder was formed into a fluidized bed by passing air at 220° F. upward through the grid. The velocity of the air as measured above the bed was 3.19 feet per second (150 cubic feet per minute). The air had sufficient velocity to buoy all of the particles of powder in a fluidized bed having an upper free surface. Heating coils located

within the bed area of the vessel were heated to 350° F. with steam.

The slurry was sprayed downward on to the bed through a two-fluid spray nozzle located 18 inches above the upper free surface of the bed. Air at 30 p.s.i. was the atomizing fluid. The slurry was pumped through the nozzle at 10 p.s.i. at the rate of 66 pounds per hour. The bed temperature was 125° F. Additional sodium dichlorocyanurate was introduced into the fluidizing vessel continuously at the rate of 23 pounds per hour. Sodium dichlorocyanurate particles with a sodium tripolyphosphate coating and containing 1.5% free moisture were continuously drawn off from the lower portion of the fluidized bed. The particles had a coating to sodium dichlorocyanurate ratio of 1:1.04 of an anhydrous basis. The thusly coated particles were continuously fed into a second fluidizing vessel having the same characteristics as the first vessel and formed into a fluidized bed. The fluidizing air had a temperature of 220° F. and a velocity of 3.82 ft. per second (180 cubic feet per minute). Steam heated coils within the bed were at a temperature of 300° F. The bed temperature was 220° F. Coated particles having no free moisture and a total moisture content of 5% were continuously drawn off from the upper part of the bed at the rate of 39 pounds per hour. (A small amount of product was lost as dust through the cyclones at the top of the fluidizing vessels.)

The final product had the following composition:

	Percent
Sodium dichlorocyanurate.....	47.90
Sodium tripolyphosphate.....	46.34
Sodium coconut oil alcohol sulfate.....	0.47
Ultramarine blue.....	0.29
Moisture (as hydrate).....	5.00

This product was a stable granular dry bleach having the outstanding characteristics described in Example I except that the particle size was greater because of the agglomeration of the coated particles resulting from the alkyl sulfate in the slurry of coating material.

In Example III, potassium dichlorocyanurate, dichlorocyanuric acid and trichlorocyanuric acid can be substituted for the sodium dichlorocyanurate in equal amounts by weight with substantially equal results except that the amounts of available chlorine in the final product will vary slightly. Moreover, sodium coconut oil alcohol glyceryl ether sulfonate, potassium laurate and sodium polypropylene benzene sulfonate (the polypropylene averaging 12 carbon atoms) can be substituted for the sodium coconut oil alcohol sulfate in equivalent amounts with substantially equal results.

The coated polychlorocyanurate particles obtained in the process of this invention are more stable and have less chlorine odor than either uncoated polychlorocyanurate particles or granular products having the same composition but dried by different processes. Other drying processes do not provide the protective coating that is obtained in the process of the present invention. This coating comprises a substantially complete film of inorganic salt around the polychlorocyanurate particles.

The coated sodium dichlorocyanurate particles obtained in Example III, uncoated sodium dichlorocyanurate and a spray dried sodium dichlorocyanurate composition were compared for relative stability. The three forms of sodium dichlorocyanurate were combined with other ingredients and had the following compositions:

- A. 35 parts of the coated sodium dichlorocyanurate particles obtained in Example III were mechanically mixed with 65 parts of a spray dried composition which contained 1.85% sodium coconut oil alcohol sulfate, 53.8% Na<sub>2</sub>SO<sub>4</sub>, 40.3% sodium tripolyphosphate, 0.15% optical brightener, 0.3% ultramarine blue and 3.6% water.
- B. 16.4 parts of uncoated sodium dichlorocyanurate were mechanically mixed with 1.5 parts sodium polypro-

pylene benzene sulfonate (the polypropylene averaging 12 carbon atoms), 41.3 parts sodium tripolyphosphate, 38.2 parts  $\text{Na}_2\text{SO}_4$ , 0.1 part optical brightener, 0.3 part ultramarine blue, 0.5 part mineral oil and 1.6 parts water.

- C. 22.5 parts of a spray dried mixture containing 67.5% sodium dichlorocyanurate and 32.5% sodium tripolyphosphate were mechanically mixed with 1.5 parts sodium polypropylene benzene sulfonate (the polypropylene averaging 12 carbon atoms), 35.2 parts sodium tripolyphosphate, 38.3 parts  $\text{Na}_2\text{SO}_4$ , 0.1 part optical brightener, 0.3 part ultramarine blue, 0.5 part mineral oil and 1.6 parts water.

Each of the three compositions was packed in a chipboard foil overwrapped carton and permitted to stand for 84 days at 120° F. and 20% relative humidity. At the end of this time the coated particles of Example III (composition A) had lost only 5.5% the original available chlorine while the uncoated particles (composition B) and the spray dried particles (composition C) lost 14% and 14.3% respectively of the original available chlorine.

The coated polychlorocyanurate particles of the present invention are useful per se as a source of available chlorine in aqueous solution for bleaching, disinfecting and sterilizing purposes. For use in the household laundry a composition containing about 5% to about 25% available chlorine is more desirable and permits the use of readily available measuring cups to measure the amount of bleaching composition that should be placed in the washing machine. Compositions containing available chlorine in this range can be obtained by using the appropriate amount of coating material in the process or a lesser amount of coating material can be used and the final dry product from the fluidized bed can be diluted with additional dry inorganic material to provide the desired available chlorine content. For example, a composition containing about 10% available chlorine can be obtained by mixing about 35 parts of the product obtained in Example III with about 65 parts of a spray-dried mixture of sodium tripolyphosphate and sodium sulfate having about the same particle size as the fluidized bleach product. A bleach containing detergent product is obtained by mixing about 20 parts of the product of Example III with about 80 parts of a conventional spray-dried, heavy-duty granular detergent.

The process of this invention is useful for coating dry chlorinated organic bleaching compounds other than the polychlorocyanurates which are preferred and which are emphasized herein because of their excellent stability and bleaching efficiency characteristics. Examples of such dry N-chlorinated organic bleaching compounds are: 1,3-dichloro-5,5-dimethyl hydantoin; N,N'-dichlorobenzoyleneurea; paratoluene sulfondichloroamide; trichloromelamine; N-chloroammeline; N-chloro succinimide; N,N'-dichloroazodicarbonamidine; N-chloro acetyl urea; N,N'-dichlorobiuret; chlorinated dicyandiamide.

What is claimed is:

1. The process of making a dry granular bleach composition comprising the steps of (1) forming a fluidized bed consisting of a dense phase bounded by an upper free surface by passing a distributed ascending current of gas at a predetermined velocity, ranging from about 1 ft./sec. to about 10 ft./sec. measured above said free surface, through a mass of solid particles of a polychlorocyanurate, having a particle size of from about 5 $\mu$  to about 5 mm., (2) heating said bed to a temperature in the range of about 100° F. to about 170° F., (3) spraying onto the particles in said bed an aqueous slurry of an inorganic coating material selected from the group consisting of sodium and potassium sulfates, phosphates, borates and carbonates to coat the particles in said bed, sufficient coating being sprayed on to obtain coated particles having a weight ratio, on an anhydrous basis, of coating material to polychlorocyanurate in the range of about 1:3

to about 5:1, said slurry containing from about 30% to about 85% water, (4) maintaining said bed in said temperature range until the free moisture content of said coated particles is from about 1% to about 15%, (5) drying said coated particles to a free moisture content of 0% to about 2% at a temperature in the range of about 190° F. to about 240° F.

2. The process of claim 1 wherein the drying of the coated particles in step (5) is effected in a fluidized bed of said particles.

3. The process of claim 2 wherein the polychlorocyanurate is selected from the group consisting of sodium and potassium dichlorocyanurates, the aqueous slurry contains from 0% to about 1.5% of an anionic organic detergent and the coating material is sodium tripolyphosphate.

4. The process of claim 2 wherein the polychlorocyanurate is selected from the group consisting of sodium and potassium dichlorocyanurates, the aqueous slurry contains from 0% to 1.5% of an anionic organic detergent and the coating material is a mixture of sodium tripolyphosphate and sodium sulfate wherein the amount of sodium sulfate is up to three times the amount of sodium tripolyphosphate.

5. The process of making a dry granular bleach composition comprising the steps of (1) forming a fluidized bed consisting of a dense phase bounded by an upper free surface by passing a distributed ascending current of air at a predetermined velocity, ranging from about 1 ft./sec. to about 10 ft./sec. measured above said free surface, through a mass of solid particles of a polychlorocyanurate having a particle size of from about 5 $\mu$  to about 5 mm. selected from the group consisting of sodium and potassium dichlorocyanurates, (2) heating said bed to a temperature in the range of 120° F. to 150° F., (3) spraying onto the particles in said bed an aqueous slurry comprising sodium tripolyphosphate and 0.5% to 1% sodium alkyl sulfate in sufficient amount to coat the particles with sodium tripolyphosphate wherein the weight ratio of the sodium tripolyphosphate coating to polychlorocyanurate, on an anhydrous basis, is in the range of 1:1.5 to 2:1, said slurry containing from about 30% to about 85% water, (4) maintaining said bed in said temperature range until the free moisture content of the coated particles is from about 1% to about 15%, (5) drying said coated particles in a fluidized bed at a temperature in the range of 205° F. to 235° F. to the complete elimination of free moisture and to a total moisture content of not less than about 2%.

6. The process of continuously making a granular bleach composition comprising the steps of (1) forming an initial fluidized bed consisting of a dense phase bounded by an upper free surface by passing a distributed ascending current of air at a predetermined velocity, ranging from about 1 ft./sec. to about 10 ft./sec. measured above said free surface, through a mass of solid particles of a polychlorocyanurate having a particle size of from about 5 $\mu$  to about 5 mm., (2) heating said bed to a temperature in the range of 120° F. to 150° F., (3) continuously spraying onto the particles in said bed an aqueous slurry of sodium tripolyphosphate to coat the particles in said bed, said slurry containing from about 30% to about 85% water, (4) continuously drawing off from the lowest portion of said bed coated particles having a weight ratio, on an anhydrous basis, of sodium tripolyphosphate to polychlorocyanurate in the range of 1:1.5 to 2:1 and having a free moisture content of about 1% to about 15%, (5) continuously supplying uncoated polychlorocyanurate particles to said bed at a point below the upper free surface of the bed to maintain said bed, (6) forming a second fluidized bed consisting of a dense phase bounded by an upper free surface by passing a distributed ascending current of air at a predetermined velocity through a mass of the coated particles being continuously drawn off from said initial fluidized bed and

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being continuously introduced into said second bed at a point in the lower portion of said bed, (7) continuously drying said coated particles in said second bed at a temperature in the range of 205° F. to 235° F. to a free moisture content of 0% to about 1%, (8) continuously drawing off from the upper portion of said second bed the dried coated particles of granular bleach.

7. The process of claim 6 wherein the polychlorocyanurate is selected from the group consisting of sodium and potassium dichlorocyanurate and the aqueous slurry contains 0.5% to 1% of sodium alkyl sulfate.

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