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GRANULAR COMPOSITIONS CONTAINING TRICHLOROCYANURIC ACID

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The present invention relates to novel granular compositions containing chlorocyanuric acid (sometimes termed chloroisocyanuric acid), and more particularly relates to dense, physically stable, granular compositions containing trichlorocyanuric acid or dichlorocyanuric acid which have improved solubility and rate of solution in water. The present invention also relates to compositions of this nature which are useful for bleaching, disinfecting, sterilizing and other purposes. In addition, the present invention relates to processes of preparing the aforementioned compositions.

Compositions consisting essentially of trichlorocyanuric acid and alkaline alkali metal salts such as alkaline alkali metal carbonates, silicates, phosphates and/or combinations of these with certain anionic wetting agents and/or synthetic detergents such as, for example, sodium salts of long chain alkyl sulfates and sodium salts of alkylated benzene sulfonic acids are described in U.S. Patent 2,607,738, issued August 19, 1952, and U.S. Reissue Patent 24,412 issued December 31, 1957, of Edgar E. Hardy. According to these patents the compositions are preferably compounded and marketed as dry powders containing the various ingredients intimately and homogeneously blended together, although these patents disclose that the mixtures may be supplied in the form of tablets, sticks, cubes, or agglomerates.

Stable compositions containing the above-mentioned ingredients and cyanuric acid or certain other organic compounds capable of being N-chlorinated which are mixed as solid particles to provide a uniform mixture of solid particles have been described in U.S. Patent 2,980,622, issued April 18, 1961, to William F. Symes. According to this patent the ingredients can be mixed to form a mixture of solid particles and then briquetted or tableted or otherwise compressed in the form of cakes, cubes, etc. These ingredients, according to this patent, can also be dissolved or slurried in water and sold as aqueous solutions or slurries or can be dried, for example, by drum drying to obtain flakes which can be used as such or ground to powder form. Such slurries can also be spray dried to form beads or hollow spheres.

However, it has since been observed that when the aforementioned compositions are placed in water under normal use conditions they do not immediately and completely dissolve. A portion of these compositions does not dissolve for prolonged periods of time but remains on the surface of the water as floating particles having the appearance of a scum, or, in some instances, settles to the bottom and remains undissolved for periods as long as five hours. It has since been found that the undissolved material in the water consists substantially of trichlorocyanuric acid and sometimes includes cyanuric acid and that the various other ingredients in the composition tend to dissolve in water at different rates. The result of this differential in the rate of solution of the various components in water causes the water, which may consist of a washing, bleaching or sterilizing bath, or water in a swimming pool, to be non-homogeneous with respect to trichlorocyanuric acid content and concentration.

Since trichlorocyanuric acid is the active available chlorine producing components of such compositions certain portions of the water bath will often contain too much or too little of such active bleaching, sterilizing or disinfecting agent prior to the final and complete solution of the trichlorocyanuric acid. In the case of a bleaching bath, the result may be inadequate bleaching of some parts of the article to be bleached or, on the other hand, damage to the article itself if contacted with the undissolved trichlorocyanuric acid per se. Where the water is that in a swimming pool, inadequate disinfection or sterilization of a volume of the pool water may result, or irritation to the eyes or skin of the users of the swimming pool may be occasioned by direct contact of such members of the swimmer with undissolved trichlorocyanuric acid.

It is one object of the present invention to provide novel compositions containing a chlorocyanuric acid wherein the chlorocyanuric acid will be rapidly dissolved in water.

It is a further object of this invention to provide a composition comprising a chlorocyanuric acid, wherein all of the components will dissolve rapidly and at substantially the same rate in water and which will overcome the hereinbefore mentioned disadvantages of the prior art compositions.

Still further advantages will become apparent from the following description and the appended claims.

The present invention provides compositions comprising dense flakes or granules of an intimate mixture of a chlorocyanuric acid, a non-chlorine containing triazine compound selected from cyanuric acid and/or alkali metal cyanurates, and an alkali metal carbonate. These granules have a bulk density as described in more detail hereinafter and are unexpectedly more soluble and more rapidly soluble and will dissolve substantially uniformly in water than a mere mixture of the same ingredients in powder form. This invention is particularly concerned with substantially dry granules, that is, granules which are not wet and are preferably either substantially water free or which contain water as water of hydration of the ingredients used. Such water of hydration when present comprises less than 10%, preferably less than 5.0%, by weight of the compositions.

The chlorocyanuric acids employed in the compositions of this invention are dichlorocyanuric acid and/or trichlorocyanuric acid, preferably trichlorocyanuric acid. Both have been described in the literature and have been referred to as possibly existing in the keto- and enol forms. These chlorocyanuric acids have very limited solubility in water but the solubility is somewhat less limited in alkaline solutions. However, chlorocyanuric acids particularly trichlorocyanuric acid, generally decompose in water, in the presence of alkaline materials (that is, significant concentrations of relatively alkaline materials or, lower concentrations of highly alkaline materials), to produce decomposition products such as NCl_3 which is a hazardous explosive and which is also toxic.

The dichlorocyanuric acid employed in the compositions of this invention has a theoretical available chlorine content of 71.66%. The commercially available product, usually containing between about 68% and 71.6% available chlorine, may also be used. Dichlorocyanuric acid is slowly and sparingly soluble in water to an extent of 0.8 gram per 100 grams of water and surprisingly the solubility does not substantially increase as the temperature of the water is increased. The trichlorocyanuric acid employed in the compositions of this invention has a theoretical available chlorine content of 91.54%. The commercially available product, usually containing between about 84% and 91.54% available chlorine, may also be used. Trichlorocyanuric acid is also slowly and sparingly soluble in water to an extent of 1.2 grams per

100 grams of water and the solubility thereof does not substantially increase as the temperature of the water is increased. The term "available chlorine" as used herein is used in the usual technical meaning as employed in the sodium hypochlorite art. The available chlorine in a given compound may be determined by analyzing for the amount of chlorine that can be liberated from the compound by treatment with an aqueous acid solution.

A variety of non-chlorine containing triazine compounds can be used in the compositions of this invention, but it has been found especially advantageous to use anhydrous cyanuric acid, alkali metal salts of cyanuric acid or hydrates of these or mixtures thereof. Of these compounds anhydrous cyanuric acid is particularly preferred. Cyanuric acid and alkali metal salts thereof have been described in the literature as crystalline materials which exist in anhydrous and hydrate forms. Cyanuric acid is sparingly soluble in water to an extent of 0.5 gram per 100 grams of water at 25° C. whereas the alkali metal salts are generally soluble (up to 10% by weight) in water.

Alkali metal salts of cyanuric acid which may be employed in the compositions of this invention include mono-, di- and/or tri-alkali metal cyanurates such as, for example, the corresponding sodium, potassium and lithium cyanurates and/or hydrates thereof. Of these, the anhydrous mono- and di-alkali metal salts of cyanuric acid have been found to be especially advantageous and anhydrous mono-sodium and di-sodium cyanurates are particularly suitable.

The alkali metal carbonates employed in the compositions of this invention include anhydrous alkali metal carbonates and/or hydrates thereof but anhydrous alkali metal carbonates including sodium, potassium and lithium carbonates are preferred. Anhydrous sodium carbonate is particularly preferred.

The proportions of the various components comprising the compositions of this invention can be varied considerably depending upon the end use of the composition. A particularly desirable composition of this invention comprises dense flakes or granules as hereinafter defined, each of which consists essentially of an intimate mixture of a chlorocyanuric acid, e.g., dichlorocyanuric acid or trichlorocyanuric acid, from about 0.05 to about 0.75 mol, per mol of the chlorocyanuric acid, of either cyanuric acid, or an alkali metal cyanurate or mixtures thereof and from about 0.25 mol to about 1.0 mol, per mol of chlorocyanuric acid of an alkali metal carbonate. The more suitable granular compositions have a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter.

When the compositions of this invention contain trichlorocyanuric acid, the amount of cyanuric acid and/or alkali metal cyanurate employed, is preferably between about 0.25 mol and about 0.75 per mol of trichlorocyanuric acid, and the amount of the alkali metal carbonate used is preferably from about 0.25 mol to about 1.0 mol, per mol of trichlorocyanuric acid. When the compositions contain dichlorocyanuric acid, instead of trichlorocyanuric acid, the amount of cyanuric acid and/or an alkali metal cyanurate used is preferably from about 0.05 mol to about 0.5 mol, per mol of dichlorocyanuric acid, and the amount of alkali metal carbonate employed is preferably usually from about 0.5 mol to about 0.75 mol, per mol of dichlorocyanuric acid. If desired the compositions may also contain mixtures of trichlorocyanuric acid and dichlorocyanuric acid, the hereinbefore defined non-chlorinated triazine compound, and an alkali metal carbonate, and the preferred relative proportions of ingredients in such compositions are within the ranges discussed in the preceding paragraph taking into account the proportions disclosed for trichlorocyanuric acid per se and dichlorocyanuric acid per se.

Surprisingly, it has presently been found that the compositions of this invention will dissolve uniformly and rapidly in those instances when the compositions are composed of dense, relatively coarse particulates such as flakes or granules wherein each particle has a density substantially corresponding to the absolute density of the mixed ingredients, e.g., an absolute density of from about 2.0 to about 2.5 grams per cubic centimeter. These coarse particulates may have almost any shape, for example, spheres, rods, platelets, flakes and the like and may also (and generally do) have an irregular shape.

The size of the coarse particulates may vary to some extent, and may consist of flat flakes or platelets having a thickness of about 4.0 millimeters to about 0.1 millimeter and a length, width, and/or other dimension of from about 0.1 millimeter up to several centimeters or more. However, the coarse particulates are usually and preferably in the form of free-flowing, irregularly shaped, coarse granules or agglomerates having a size such that the largest dimension of any granule or agglomerate is not more than about 4.0 millimeters, and is preferably in the range of about 0.8 millimeter to about 4.0 millimeters. The smallest dimension of at least 90% by weight of the granules is not less than 0.1 millimeter, and is preferably in the range of about 0.1 to about 0.25 millimeter.

Stated differently the preferred granular compositions of this invention are composed of dense, coarse, irregularly shaped granules having a particle size range and particle size distribution such that all or substantially all of the granules, in a dry state, will pass through a No. 5 mesh U.S. Standard screen and at least 90% by weight of the granules will be retained on a No. 140 mesh U.S. Standard screen. The granular compositions which are particularly desirable and preferred are composed of dense, coarse irregularly shaped granules having a size range and distribution such that all or substantially all of the granules will pass through a No. 20 mesh U.S. Standard screen and at least 90 percent by weight of the granules will be retained on a No. 60 mesh U.S. Standard screen.

The granular compositions of this invention composed of coarse free flowing granules, having a particle size within the above defined ranges, preferably also have a bulk density in the range of from about 0.85 gram to about 1.0 gram per cubic centimeter. On the other hand each individual granule in such preferred compositions has an absolute density of from about 2.0 to 2.5 grams per cubic centimeter. The term "bulk density" is used herein in its generally understood meaning, that is, the weight per unit volume of a solid, dry, flowable material which has not been substantially compacted after introduction of the material, usually by pouring, into a volumetrically calibrated vessel, such as a graduate.

The compositions of this invention which preferably comprise dense water soluble granules of an intimate mixture of a chlorocyanuric acid, cyanuric acid and/or alkali metal salts thereof and alkali metal carbonates as hereinbefore described can be mixed with powdered particles or granules of neutral to alkaline water soluble inorganic salts other than carbonates, and/or particles or granules of certain surface active agents. Alternatively such neutral to alkaline inorganic salts and/or surface active agents may be incorporated into the dense granules of the above described granular compositions.

In addition to the alkali metal carbonates hereinbefore described a variety of alkaline, water soluble, alkali metal salts may be mixed with, or, when desirable, incorporated into the granules of the granular compositions of this invention. Such salts preferably include these inorganic salts which are employed as detergent builders. Examples of these salts are tri-alkali metal phosphates such as trisodium phosphate and tripotassium phosphate; di-alkali metal hydrogen phosphates such as disodium and dipotassium hydrogen phosphates; the alkaline, water-soluble molecularly dehydrated alkali metal phosphate salts such as the alkali metal pyrophosphates, for example, tetrasodium pyrophosphate, trisodium hydrogen pyrophosphate and tetrapotassium pyrophosphate, also

the alkali metal tripolyphosphates such as sodium tripolyphosphate ($Na_5P_3O_{10}$) and potassium tripolyphosphate, the alkaline water soluble alkali metal metaphosphates such as sodium hexametaphosphate; the water soluble alkali metal silicates such as sodium silicates having an Na_2O to SiO_2 mol ratio of 1.5:1 to 1:3.5, preferably 1:1 to 1:3.5 and the corresponding potassium silicates; the water soluble alkali metal borates such as calcined sodium tetraborate or borax. The preferred salts are those which do not undergo any or substantially any oxidation-reduction reaction with the chlorocyanuric acids.

The above mentioned salts may be used alone or in various combinations with each other or with water soluble, neutral, inert diluents which may also have some detergent building properties, for example water soluble, neutral, inert, inorganic alkali metal salt diluents such as neutral alkali metal sulfates or chlorides, for example, sodium sulfate or sodium chloride.

The proportions of such alkaline and/or neutral salts employed in the compositions of this invention can be varied considerably depending upon the composition desired and/or the end use of the composition. When it is desired to mix such salts as particles with the hereinbefore described dense, granular compositions such salts may constitute from about 40% to 96% by weight of the composition. Of this the alkaline alkali metal salts may comprise from about 10 to about 90% by weight of the total salts and the inert diluent salt is usually employed in amounts ranging from 90% to 10% of such salts. When it is desired to incorporate the above salts into the above described granules the amounts of such salts in the granules may be generally as above described.

Although the compositions of this invention comprise dense granules of an intimate mixture of a chlorocyanuric acid, cyanuric acid or an alkali metal cyanurate and an alkali metal carbonate and may include the above described alkaline salts, inert diluent salts or combinations thereof, the compositions may also contain relatively minor amounts, usually less than 15% by weight on a solids basis, preferably 1% to 10% by weight, of anionic wetting agents or synthetic detergents such as those described in the above mentioned Symes Patent 2,980,622. Such agents or detergents include organic surface active sulfonates or sulfates having a hydrophobe and hydrophile portion, the latter being a sulfate or a sulfonate group, for example, sodium salts of long chain alkyl sulfates, sodium salts of alkyl naphthalene sulfonic acids, sodium salts of alkyl benzene sulfonic acids particularly those in which the alkyl group contains from about 8 to 20 carbon atoms, sodium salts of sulfonated mineral oils, and sodium salts of sulfosuccinic esters such as sodium dioctyl sulfosuccinate. These detergents may be mixed with the salts and the resulting mixture mixed with the granules hereinbefore described, or, alternatively, the detergents can be incorporated directly into the granules of the granular compositions with or without the aforementioned inorganic alkaline salts and inert diluent salts.

The various ingredients referred to herein can be used in the compositions in various proportions depending upon whether the composition is to be used as a bleaching composition, a disinfecting composition, a dishwashing composition, a detergent composition, etc. However, in general, the granular compositions will contain from about 0.5% to about 70% by weight of a chlorocyanuric acid, from about 0.05 to 0.75 mol, per mol of chlorocyanuric acid of either cyanuric acid or an alkali metal cyanurate or mixtures thereof and from about 0.25 mol to about 1.0 mol, per mol of chlorocyanuric acid, of an alkali metal carbonate. Such granules may also contain from about 0.05% to about 10% by weight of anionic wetting agent, when used, and the remainder of the granules may contain, when desired, up to 85% by weight of the total granular composition of the aforementioned alkaline metal salts and/or inert neutral diluent salts.

As noted hereinbefore, it is not necessary that the organic surface active agent or such salts be incorporated in the granules and these materials can be mixed as powdered particles or granules with the dense granules of a chlorocyanuric acid, a triazine compound and an alkali metal carbonate as hereinbefore described. When all of the ingredients are incorporated in the granules of the granular compositions of this invention such granules usually have the particle size range and the absolute density and bulk density range of the granules hereinbefore described. These compositions whether in dense granular form or in the form of mixtures of solid particles and dense granules are characterized in being uniformly and rapidly soluble in water as will be hereinafter evident.

In one embodiment of this invention the compositions comprise dense granules containing from about 40% to 80% by weight of a chlorocyanuric acid from about 30% to 7% by weight of cyanuric acid or an alkali metal salt thereof and from about 30% to about 13% by weight of alkali: metal carbonate. Each of the granules of the compositions preferably have an absolute density of from about 2.0 to 2.5 grams per cubic centimeter. The granules also have a particle size within the range hereinbefore described and the granular compositions have a bulk density of from about 0.85 to 1.0 gram per cubic centimeter. Such compositions contain from 25% to 75% preferably from about 40% to about 65% of available chlorine and are particularly useful in bleaching operations or sanitizing water in swimming pools.

In a further embodiment of this invention the compositions comprise dense granules containing from about (1) 3% to 15% by weight of a chlorocyanuric acid, (2) from about 0.1% to about 5.0% of cyanuric acid or an alkali metal salt thereof (3) from about 0.9% to about 11.0% by weight of an alkali metal carbonate and (4) from about 96% to about 76% by weight of one or a combination of several of the hereinbefore described neutral to alkaline alkali metal salts other than an alkali metal salt thereof, (3) from about 0.9% to sitions usually have an absolute density of from about 2.0 to about 2.5 grams per cubic centimeter. The granules have a particle size in the range hereinbefore described and the compositions usually have a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter. These compositions contain from about 1.5 to 10% available chlorine and are useful as household bleaches and sanitizers.

In another embodiment of this invention the compositions comprise dense granules containing (1) from about 3% to 15% by weight of chlorocyanuric acid, (2) from about 0.1 to 5.0% by weight of cyanuric acid or an alkali metal salt thereof, (3) from about 0.9% to 4.0% by weight of an alkali metal carbonate, (4) from about 95% to 61% by weight of one or a combination of several of the above described neutral to alkaline alkali metal salts, other than carbonates, and from about 1% to 15% by weight of an organic surface active agent of the kind described. The granules of such compositions have a bulk density of about 2.0 to about 2.5 grams per cubic centimeter. The granules also preferably have a particle size in the range hereinbefore described and the granular compositions have a bulk density of from about 8.5 to about 1.0 grams per cubic centimeter. These compositions contain from about 1.5% to about 10% by weight of available chlorine and are useful in home laundering and dishwashing operations.

In accordance with another embodiment of this invention the compositions comprise dense granules containing from about 39.5% to 68% by weight of a chlorocyanuric acid, from about 30% to 6% by weight of cyanuric acid or an alkali metal salt thereof and from about 29.5% to 11% by weight of an alkali metal car-

bonate and from about 1% to 15% by weight of an organic surface active agent of the kind hereinbefore described. These compositions contain from about 25% to 65% available chlorine. The granules of these compositions have absolute densities, and bulk densities within the ranges described for the compositions of this invention. The granular compositions have a bulk density within the ranges described for the compositions comprising the other embodiments of this invention.

If desired the neutral to alkaline alkali metal salts, other than the alkali metal carbonates, and the organic surface active agents may be mixed as solid particles with dense granules containing the chlorocyanuric acid, cyanuric acid or an alkali metal salt thereof and an alkali metal carbonate and having particle sizes, absolute densities, and bulk densities within the ranges hereinbefore described. Such compositions contain ingredients in the proportions above described and will dissolve rapidly and uniformly in water.

In most instances the proportions and kind of ingredients in the formulation will depend on the purpose for which the formulation or composition is being used, that is, whether it is to be used for bleaching, sanitizing, dishwashing, etc. Irrespective of the use involved, dense granules of the proper particle size and density and containing the chlorocyanuric acid, cyanuric acid or alkali metal cyanurate and alkali metal carbonate in the proper proportions dissolve much more rapidly (e.g. in one fifth of the time) and more uniformly in water than powdered, or tableted, or agglomerated compositions described in the prior art.

The compositions of this invention may be prepared in various ways. One particularly suitable process comprises intimately mixing the ingredients thereof as dry or substantially dry (e.g., containing less than 10% water as water of hydration or being water-free) as finely divided particles or as powders. Thereafter the resulting mixture is compressed at a pressure and for a time sufficient to increase the bulk density of the mixture at least 0.05, preferably at least 0.1 and up to 0.3, gram per cubic centimeter more than the bulk density of the mixture prior to compression and the compressed mixture has an absolute density of from about 2.0 to about 2.5 grams per cubic centimeter. In a preferred process the mixture is compressed from a bulk density of from about 0.7 to 0.75 gram per cubic centimeter to about 0.85 to 1.0 gram per cubic centimeter and the solid compressed mixture has an absolute density of from about 2.0 to 2.5 grams per cubic centimeter. A suitable starting mixture (before compression) may, for example, have a bulk density of from about 0.70 to about 0.75 gram per cubic centimeter. If the resultant solid mass or product does not have particles of the desired particle size, such mass or product may be, and preferably is, comminuted to form particles having a particle size such that the bulk density of the ground compressed product will usually be between 0.85 to 1.0 gram per cubic centimeter. The terms "finely divided particles" or "powders" as used herein are intended to mean and to refer to particles having a size such that the largest dimension of the particles is substantially not more than 70 microns and may be below 40 microns. Stated differently all or substantially all of such powders will pass through a No. 200 mesh U.S. Standard screen and will preferably pass through a No. 325 U.S. mesh standard screen.

The various powdered ingredients employed in making the compositions of this invention are preferably uniformly and intimately admixed prior to compression. Such uniformity of mixing is especially necessary if the compressed product is to dissolve rapidly and uniformly in water. The mixing of the powdered ingredients is preferably carried out mechanically and may be accomplished in a number of ways commonly employed in the mixing of dry or substantially dry materials such as for example by stirring, tumbling, mulling, or the like. The materials so admixed usually produce a dry light flowable powder having a bulk density of about 0.7 to 0.75 gram cubic centimeter and are suitably compacted or compressed as described hereinafter.

The various powdered mixtures, prepared as above described, may be compressed or densified in a variety of ways for example by employing hydraulic presses such as a Carver press, or a high pressure "sheet press" or a press consisting of cylindrical rolls between which the powders may be fed and compressed. As noted hereinbefore, it has been found particularly desirable to compress or densify the mixtures to a density of from about 2.0 to 2.5 grams per cubic centimeter which is usually substantially the absolute density of the composition. Stated differently it is preferred that the powdered mixtures be compressed uniformly and to the maximally obtainable density prior to comminuting or granule formation. Hence it has been found especially advantageous to subject relatively thin layers of the powdered material to pressures ranging from between about 5,000 to 50,000 pounds per square inch until the material has been maximally and uniformly compressed.

In compressing the powdered mixtures it has been found especially desirable to pass the mixtures between abutting rotary cylinder rolls which cylinders can be subjected to thrusts up to 50,000 pounds. As the powder passes between the rolls it is subjected to pressures of from about 3,000 to 15,000 pounds per linear inch equivalent to a pressure of about 24,000 to about 120,000 pounds, per square inch. The compressed material so obtained is a friable sheet of a compressed composition which usually breaks into flakes of varying sizes but which usually have a thickness of from 0.1 to 4.0 millimeters. These flakes can then be ground or comminuted to form particles having the particle size and bulk density hereinbefore described for the granules of this invention. In some instances it may be desirable to precompress the material and this may be suitably accomplished by pelleting or tableting the materials in a commercial tableting press or a Carver hydraulic press. Such pre-compressed materials generally are not uniformly compressed and have densities below the densities required to accomplish the desired results. However, such materials may be ground to granular or powdered form and be suitably densified or compressed by passing it through the cylindrical rolls as above described. The comminution or grinding of the compressed material may be suitably accomplished by well-known methods such as by mechanically abrading the flakes or platelets through a screen of pre-determined pore size, or by tumbling in the presence of large spherical solids such as glass marbles or beads. The compositions advantageously and are preferably comminuted by mechanically abrading the materials through one or more coarse screens for example a No. 3 or No. 4 mesh U.S. Standard screen. The material so comminuted usually comprises particles having various sizes, e.g. some of the particles will be retained on a No. 20, 40, 60, 80, 100, 120 and 140 mesh screens, and up to about 10% by weight of such material may be in powdered form, that is, will pass through a No. 200 mesh screen. If desirable such powdered material may be separated by screening or by compressed air. Preferably the comminuted particles are screened so that substantially all the granules of the composition will pass through a No. 4 mesh, preferably a No. 20, mesh standard U.S. screen and will be retained on a No. 140, preferably a No. 60, mesh standard U.S. screen.

The compositions of this invention having the particle size distribution described in the preceding paragraph including compositions containing less than 10% by weight of particles which pass through a No. 140 mesh standard U.S. screen, will usually have a bulk density of about 0.85 to about 1.0 gram per cubic centimeter. Granular compositions having a particle size such that

all or substantially all of the granules will pass through a No. 20 mesh screen and at least 90% by weight of the granules will be retained on a No. 60 mesh screen usually have a bulk density of from about 0.90 to about 0.95 gram per cubic centimeter.

In the past, granules or agglomerates have generally been prepared by incorporating adhesive materials including casein, gelatin, starch, acacia and the like into the mixture or composition to be granulated. These adhesive materials, commonly referred to as "binders" are usually mixed with the particles of the other materials in the presence of up to 20% water or other liquids to produce a wet mass which is then dried and ground to the desired particle size. Granules so-produced usually have a bulk density of below 0.6 usually below 0.5 gram per cubic centimeter.

In accordance with the processes of the present invention it has been found possible to obtain granules or agglomerates without employing water or other "binders." The elimination of water, in the granulation process of the present invention is particularly advantageous due to the instability of the chlorocyanuric acids in the presence of moisture.

As a general rule, finely divided solid particles will usually dissolve more rapidly in a solvent such as water than will coarse solid particles of the same material. It would therefore be expected that compositions composed of finely divided solid particles (powders or finely ground materials) would dissolve more rapidly than coarser particles. However, when compositions containing the chlorocyanuric acid, the unchlorinated triazine and the carbonate are in loose coarse or in loose powdered form, or alternatively when these compositions are compressed or tableted in accordance with procedures commonly employed for such purposes, the compositions are slowly soluble in water and a long period of time is required for complete solution due to the relative insolubility and slow rate of solution of the chlorocyanuric acids.

It presently has been observed that when granules have an absolute density below the absolute density of the mixture, the bulk density of the granular compositions correspondingly decreases. If the bulk density is decreased to below 0.85 gram per cubic centimeter the granular compositions usually do not dissolve uniformly in water and some of the chlorocyanuric acid settles to the bottom of the vessel as a powder and/or floats on top of the water (where it appears as a "scum") for periods up to 5 hours. It has also been observed that when the dense granules having an absolute density between 2.0 and 2.5 grams per cubic centimeter are ground or comminuted to granules having a particle size such that all or substantially all of the granules pass through a No. 140 mesh U.S. screen, the components of such granules will not dissolve uniformly and some of the chlorocyanuric acid component remains undissolved as above described.

The ingredients of such powdered compositions generally do not dissolve uniformly in water, the chlorocyanuric acid remaining undissolved for periods up to 5 hours as above described. When the ingredients are in a compressed form such as a tablet or briquette having an absolute density somewhat below 2.0 grams per cubic centimeter the tablets or briquettes usually do not dissolve uniformly in water and the chlorocyanuric acid remains undissolved for prolonged periods of time.

When the ingredients are mixed as powders, as taught in the prior art the resulting mixtures have a bulk density of between about 0.70 to 0.75 gram per cubic centimeter. When such mixtures are immersed in water they do not dissolve for prolonged periods of time and the components of the mixtures are not uniformly soluble in water.

A further understanding of the invention will be obtained from the following specific examples which are intended to illustrate the invention but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

EXAMPLE I

Dry granular compositions, containing the ingredients listed in Table I in the stated proportions, and having a bulk density in the range of 0.85 to 1.0 gram per cubic centimeter and a particle size such that all of the granules passed through a 5 mesh screen and 90% by weight of the granules remained on a 140 mesh screen were prepared.

The granular compositions were prepared by mixing the ingredients, as powders, in the proportions stated in Table I in an eight-quart Baker-Perkins folding mixer. The mixing blades of the mixer were rotated at 24 r.p.m. and the particulated ingredients were mixed for thirty minutes. Each ingredient was in powdered form and consisted of particles all of which passed through a 200 mesh standard screen. After mixing, the powdered mixtures were screened on a Ro-tap analyzer. The particles were found to have a size such that all of the particles of the powdered mixtures passed through a 200 mesh U.S. Standard screen and about half of the mixture of particles passed through a number 325 mesh screen. Available chlorine analyses were conducted on the mixtures that were retained on the number 325 mesh screen and on the mixtures that passed through that screen.

Table I

Composition Number	1	2	3	4	5	6	7	8
Ingredient:								
Trichlorocyanuric acid	61.8	0	64.4	67.3	0	0	58.1	0
Dichlorocyanuric acid	0	69.9	0	0	68.5	67.3	0	66.1
Cyanuric acid	17.1	11.4	0	0	0	0	16.1	10.8
Monosodium cyanurate	0	0	20.9	0	13.1	0	0	0
Disodium cyanurate	0	0	0	15.0	0	14.7	0	0
Sodium carbonate	21.1	18.7	14.7	17.7	18.4	18.0	0	0
Potassium carbonate	0	0	0	0	0	0	25.8	23.1
Available chlorine (percent)	55.0	49.3	57.3	59.8	48.3	47.4	51.6	46.6

Such analyses showed that both powdered mixtures had substantially the same available chlorine content. The bulk-density of the powdered mixtures (determined by funneling the mixtures into a 100 milliliter tared graduate and weighing the graduate when it contained 100 milliliters by volume of the mixtures) are listed in Table II along with the particle size of the particles of the powdered mixtures. It is evident from this table that the bulk density of the powdered compositions tend to decrease as the size of the particles in the compositions decrease.

Table II

Powdered mixtures corresponding to Composition No.	*Particle size	Bulk density, gms./cc.	Solution time (seconds)
1	−200 mesh	0.74	320
2	−200 mesh	0.73	300
3	−325 mesh	0.70	360
4	−325 mesh	0.70	380
5	−200 mesh	0.75	290
6	−200 mesh	0.74	280
7	−325 mesh	0.71	480
8	−325 mesh	0.72	430

*Numbers refer to standard U.S. screens.

The compositions so mixed were compressed and compacted by feeding the powders between rotating stainless steel rolls of a Model SN Chilsonater, manufactured by the Fitzpatrick Company, 1001 W. Washington Blvd., Chicago, Illinois. The stainless steel rolls were rotated at a speed of 9 r.p.m. and were operated at a "thrust" or pressure of 20,000 lbs. The powdered compositions were thus subjected to a pressure of 3000 pounds per linear inch or a pressure equivalent to about 48,000 pounds per square inch. The compressed powder was discharged from the rolls in the form of a sheet or ribbon 20 centi-

meters wide and 1.0 mm. thick which fractured, as it increased in length, into flake of varying sizes. The density of the flakes of each composition was measured and found to be from 2.0 to 2.5 grams per cubic centimeter depending upon the particular composition. The compositions having the greater quantity of metal carbonate had the higher densities within these ranges.

The flakes of the compacted compositions were then comminuted to granules by tumbling in a rotary ball mill, containing ½ inch diameter hard rubber balls, for a period of 15 minutes after which time the compositions were removed and passed through selected screens to obtain granules having the desired particle size. Bulk densities were determined as hereinbefore described for these granular compositions containing the ingredients described in Table I. These values including particle sizes and bulk densities are included in Table III.

Table III

Composition No.	Granular size*	Granular Bulk Density, gms./cc	Solution time (seconds)
1	−10 mesh+80 mesh	0.85	55
2	−8 mesh +100 mesh	0.91	58
3	−20 mesh+60 mesh	0.95	50
4	−20 mesh+60 mesh	0.94	51
5	−20 mesh+60 mesh	0.93	46
6	−20 mesh+60 mesh	0.94	56
8	−20 mesh+60 mesh	0.94	60

*Numbers refer to U.S. Standard screens.

The solution times of various of these granular compositions were determined by adding 5 grams of a powdered composition to 1000 ml. of water, maintained at 25° C. and stirring the mixture until the composition had completely dissolved. The solution times of various compositions are included in Table III along with the particle sizes and bulk densities of the compositions.

Solution times were also determined as above described except that the aqueous dispersions were not agitated. Under these conditions about 10 minutes were required for the granular compositions to completely dissolve in the water. In all instances the dense granular compositions dissolved uniformly and rapidly in water and in no case did the chlorocyanuric acid appear in the form of a "scum" or settle to the bottom of the water. Where the water was not agitated, all the granular materials had dissolved within 10 minutes. By way of contrast powdered mixtures which were not compressed did not completely dissolve in water for periods of from 1 to 5 hours.

EXAMPLE II

Twenty parts of the various granular compositions identical to the granular compositions described in Table III were tumbled, with 80 parts of a powdered mixture (e.g., having particles of a size such that 50% by weight of the particles passed through a No. 200 mesh screen) containing 35% by weight of sodium tripolyphosphate and 65% by weight of anhydrous sodium sulfate. Various other compositions containing the above described granular compositions were prepared by tumbling the granules (twenty parts of the granules) with 80 parts of a powdered mixture having the particle size as above mentioned and containing 35% by weight of tetrasodium pyrophosphate, 60% by weight of anhydrous sodium sulfate at 5% by weight of sodium dodecylbenzene sulfonate with 20% by weight of the granular compositions.

All of the compositions so prepared consisted of uniform mixtures of the granular compositions, wherein the granules retained their original size, and powdered materials. Solution times were determined as described in Example I. In all instances each of these compositions dissolved uniformly and within substantially the same times as the granular compositions of Table III of Example I.

EXAMPLE III

Granular compositions, described in Table IV were prepared by intimately and thoroughly mixing the ingredients as powders and in the dry state and thereafter compacting and granulating the mixtures as described in Example I and separating those granules having a particle size such that all of the granules passed through a No. 20 mesh U.S. Standard screen and were retained on a No. 60 mesh screen. The granular compositions so prepared had bulk densities similar to the granular compositions 1 through 8 (described in Table III) and had solution times comparable to the solution times of such compositions. Similar compositions containing from 1% to 10% by weight of sodium dodecylbenzene sulfonate were also prepared with substantially the same results.

All of the compositions hereindescribed were stored several months under ambient conditions and checked for loss of available chlorine. During this period there was no appreciable loss of available chlorine in any of the compositions.

Table IV

Composition Number	9	10	11	12	13	14
Ingredients:						
Trichlorocyanuric acid	10.0	10.0	10.0			
Dichlorocyanuric acid				10.0	10.0	10.0
Cyanuric acid	2.8	2.8	2.8	1.6	1.6	1.6
Sodium carbonate	3.4	3.4	3.4	2.7	2.7	2.7
Sodium tripolyphosphate	27.9	18.5			19.0	31.0
Tetrasodium pyrophosphate			32.0	28.6		
Anhydrous sodium metasilicate		18.5			19.0	
Anhydrous sodium sulfate	55.9		51.8	57.1	47.7	54.7
Sodium chloride		46.8				

Compositions 1 through 8, in granular form, are particularly useful for chlorinating the water in swimming pools to maintain the sanitized conditions required by public health laws. The compositions described in Examples II and III can be variously used in sanitizing containers in food processing operations, in bleaching processes, or in dish-washing or laundering procedures. All of the compositions were uniformly and rapidly soluble in water. On the other hand tablets, briquettes or spray-dried particles or powdered mixtures containing the ingredients hereindescribed do not uniformly dissolve in water. Complete solution of such mixtures in water requires from 6 to 30 times longer than the time required for the compositions of the present invention herein described.

What is claimed is:

1. A water-soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of (1) a chlorocyanuric acid selected from the group consisting of trichlorocyanuric acid and dichlorocyanuric acid, (2) from about 0.05 to about 0.75 mol, per mol of said chlorocyanuric acid, of a triazine compound selected from the group consisting of cyanuric acid and alkali metal cyanurates and (3) from about 0.25 to about 1.0 mol, per mol of said chlorocyanuric acid, of an alkali metal carbonate, said granular composition being further characterized in having a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter and in that at least 90% of the granules of the composition have a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.1 millimeter.

2. The composition as in claim **1**, wherein (1) the chlorocyanuric acid is trichlorocyanuric acid, (2) the triazine compound is cyanuric acid and (3) the alkali metal carbonate is sodium carbonate.

3. The composition as in claim **1**, wherein (1) the

chlorocyanuric acid is trichlorocyanuric acid, (2) the triazine is a sodium cyanurate and (3) the alkali metal carbonate is sodium carbonate.

4. A water-soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of (1) trichlorocyanuric acid, (2) from about 0.25 to about 0.75 mol, per mol of trichlorocyanuric acid, of cyanuric acid and (3) from about 0.75 to about 1 mol, per mol of trichlorocyanuric acid, of sodium carbonate, said granular composition having an available chlorine content of from about 40% to about 65% of available chlorine and a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter, and being further characterized in that at least 90% of the granules of said granular composition have a size such that the largest dimension of the granules is not more than about 0.8 millimeter and the smallest dimension of the granules is not less than about 0.25 millimeter and not more than 10% by weight of the granules have dimensions smaller than 0.25 millimeter.

5. A water-soluble granular composition consisting essentially of (a) dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of (1) a chlorocyanuric acid selected from the group consisting of trichlorocyanuric acid and dichlorocyanuric acid (2) from about 0.05 to about 0.75 mol, per mol of said chlorocyanuric acid of a triazine compound selected from the group consisting of cyanuric acid and alkali metal cyanurates and (3) from about 0.25 to about 1 mol, per mol of said chlorocyanuric acid, of an alkali metal carbonate, and the balance of said composition consisting essentially of (b) a water-soluble, inert, neutral to alkaline inorganic salt selected from the group consisting of alkali metal phosphates, silicates, sulfates and chlorides, said composition being further characterized in having a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter and in that at least 90% of the aforesaid granules of the composition have a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is no less than about 0.1 millimeter.

6. A water soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consist essentially of an intimate mixture of (1) from about 3% to 15% by weight of trichlorocyanuric acid, (2) from about 0.1% to about 5% by weight of cyanuric acid, (3) from about 0.9% to about 11% by weight of sodium carbonate and (4) from about 96% to about 76% by weight of a mixture consisting essentially of sodium tripolyphosphate and anhydrous sodium sulfate, said composition being further characterized in having a bulk density of about 0.85 to about 1.0 gram per cubic centimeter and in that at least 90% of the granules have a largest dimension of not more than 4.0 millimeters and a smallest dimension of not less than 0.1 millimeter.

7. A water-soluble granular composition consisting essentially of:

(a) dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consist essentially of an intimate mixture of (1) trichlorocyanuric acid, (2) from about 0.25 to about 0.75 mol, per mol of trichlorocyanuric acid, of cyanuric acid and (3) from about 0.75 to 1.0 mol, per mol of trichlorocyanuric acid, of sodium carbonate,

(b) from about 1 to 15% by weight of an organic surface active agent selected from the group consisting of organic surface active sulfonates and sulfates having a hydrophobe and hydrophile portion, and

(c) the balance of said composition consisting essentially of a water-soluble, inert, neutral to alkaline inorganic salt selected from the group consisting of alkali metal phosphates, silicates, sulfates and chlorides;

said composition being further characterized in having a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter and in that at least 90% of the aforesaid granules of said composition have a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.1 millimeter.

8. A water-soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of:

(1) from about 3% to 15% by weight of trichlorocyanuric acid,

(2) from about 0.1 to 5% by weight of cyanuric acid,

(3) from about 0.9 to 4% by weight of sodium carbonate,

(4) from about 1 to 15% by weight of the sodium salt of an alkylbenzene sulfonic acid having from 8 to 20 carbon atoms in the alkyl group, and

(5) from about 95 to 61% by weight of a mixture consisting essentially of sodium tripolyphosphate and anhydrous sodium sulfate;

said composition being further characterized in having a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter and in that at least 90% of the aforesaid granules of said composition have a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.1 millimeter.

9. A process for preparing a granular composition of granules, which dissolve rapidly and uniformly in water, which consists essentially in the steps of (1) mixing (a) particles of a chlorocyanuric acid selected from the group of trichlorocyanuric acid and dichlorocyanuric acid, (b) from about 0.05 to about 0.75 mol, per mol of said chlorocyanuric acid, of particles of a triazine compound selected from the group consisting of cyanuric acid and alkali metal cyanurates, and (c) from about 0.25 to about 1 mol, per mol of said chlorocyanuric acid, of particles of an alkali metal carbonate, the aforesaid particles having a size such that substantially all of the particles will pass through a No. 200 mesh U.S. Standard screen, (2) compressing the mixture from step (1) into the form of a solid shape having a bulk density of about 0.85 to about 1.0 gram per cubic centimeter and an absolute density of about 2.0 to about 2.5 grams per cubic centimeter, (3) comminuting said solid form to form granules, and (4) separating from the resulting comminuted material granules having a size such that the largest dimension of at least 90% of the separated granules is not more than about 4.0 millimeters and the smallest dimension is not less than about 0.1 millimeter.

10. A process for preparing a granular composition of granules, which dissolve rapidly and uniformly in water, which consists essentially in steps of (1) mixing (a) particles of trichlorocyanuric acid, (b) from about 0.25 to about 0.75 mol, per mol of trichlorocyanuric acid, of particles of cyanuric acid, and (c) from about 0.75 to about 1.0 mol, per mol of trichlorocyanuric acid, of particles of sodium carbonate, the aforesaid particles having a size such that substantially all of the particles will pass through a No. 200 mesh U.S. Standard screen, (2) compressing the mixture from step (1) into the form of a solid sheet having a bulk density of about 0.85 to about 1.0 gram per cubic centimeter and an absolute density of about 2.0 to about 2.5 grams per cubic centimeter, (3) comminuting said solid sheet to form granules, and (4) separating from the resulting comminuted material granules having a size such that the largest dimension of at least 90% of the separated granules is not more than about 0.4 millimeter and the smallest dimension is not less than about 0.1 millimeter.

11. A process for preparing a granular composition of granules, which dissolve rapidly and uniformly in water, which consists essentially in steps of (1) mixing (a) particles of trichlorocyanuric acid, (b) from about 0.25 to about 0.75 mol, per mol of trichlorocyanuric acid, of particles of sodium cyanurate, and (c) from about 0.25 to about 1.0 mol, per mol of trichlorocyanuric acid, of particles of sodium carbonate, the aforesaid particles having a size such that substantially all of the particles will pass through a No. 200 mesh U.S. Standard screen, (2) compressing the mixture from step (1) into the form of a solid sheet having a bulk density of about 0.85 to about 1.0 gram per cubic centimeter and an absolute density of about 2.0 to about 2.5 grams per cubic centimeter, (3) comminuting said solid sheet to form granules, and (4) separating from the resulting comminuted material granules having a size such that the largest dimension of at least 90% of the separated granules is not more than about 0.4 millimeter and the smallest dimension is not less than about 0.1 millimeter.

12. A water soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of trichlorocyanuric acid from about 0.25 mol to about 0.75 mol, per mol of trichlorocyanuric acid, of mono-sodium cyanurate and from about 0.5 mol to about 0.75 mol, per mol of trichlorocyanuric acid, of sodium carbonate, said granular composition being characterized in having an available chlorine content of from about 40% to about 65% of available chlorine and a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter, at least 90% by weight of the granules of said granular composition having a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.1 millimeter.

13. A water-soluble granular composition consisting essentially of dense, water-soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of trichlorocyanuric acid, from about 0.25 mol to about 0.75 mol, per mol of trichlorocyanuric acid, of di-sodium cyanurate and from about 0.25 mol to about 0.5 mol, per mol of trichlorocyanuric acid, of sodium carbonate, said granular composition being characterized in having an available chlorine content of from about 40% to about 65% of available chlorine and a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter, at least 90% by weight of the granules of said granular composition having a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.1 millimeter and not more than 10% by weight of the granules having smaller dimensions.

14. A water-soluble granular composition consisting essentially of dense water soluble granules that are rapidly and uniformly soluble in water and each of which consists essentially of an intimate mixture of dichlorocyanuric acid, from about 0.05 mol to about 0.5 mol, per mol of dichlorocyanuric acid, of cyanuric acid and from about 0.5 mol to about 0.75 mol, per mol of dichlorocyanuric acid, of sodium carbonate, said granular composition having a bulk density of from about 0.85 to about 1.0 gram per cubic centimeter; at least 90% by weight of the granules of said granular composition having a size such that the largest dimension of the granules is not more than about 4.0 millimeters and the smallest dimension of the granules is not less than about 0.25 millimeter.

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