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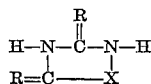
**COMPOSITIONS FOR AND PROCESSES OF BLEACHING TREATED TEXTILES**

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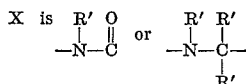
15 Claims

**ABSTRACT OF THE DISCLOSURE**

Compositions comprising an intimate mixture of about one molecular proportion of polychlorocyanurate having an alkali metal or alkaline metal earth cation in its molecular structure with from about 0.5 to 6 molecular proportions of an organic compound having in one tautomeric form the structural formula



where



R is oxygen or NH, and R' is hydrogen or an alkyl radical having from 1 to 10 carbon atoms provide effective bleaching of textiles treated with polymeric materials containing NH groups with little or no textile damage.

The present invention generally relates to novel processes for bleaching treated textiles and more particularly relates to bleaching compositions containing a polychlorocyanurate, hereinafter defined, and which are useful for bleaching treated textiles. Such compositions are particularly adapted to be used in aqueous media to bleach textiles without substantial reduction in tensile strength and color fading and to provide improved "brightening" or "whiteness." The present invention further relates to an improved process for bleaching textiles particularly those which comprise fibers or filaments containing organic polymers having imide or amide groups.

It is well known in the art that sodium hypochlorite bleaching and disinfecting compositions are very effective and have found widespread acceptance when packaged and sold in the form of aqueous solution. However, because these must be dispensed as liquids and are relatively dilute, there has been a trend toward the development of compounds packaged in the form of dry powders that have similar bleaching and antiseptic properties, because for certain special purposes they are more convenient to handle, package and ship. Calcium hypochlorite was one of the first compounds proposed as a component of a dry bleach composition. Although this compound provides bleaching and disinfecting properties when dissolved in water, the calcium ion introduces additional hardness to the water, and the concentrated solutions required for removing stains from fabrics produce a heavy sediment. In addition, the resultant precipitate of calcium carbonate (from hard water) usually contains occluded hypochlorite which deposits on the clothes during washing and remains to cause damage when the hypochlorite decomposes.

The aforementioned disadvantages have been overcome in the art with the utilization, for example, of certain polychlorocyanurates in bleaching formulations in place of the hypochlorite compounds to provide the required "available chlorine." Various polychlorocyanurates, which have been suggested for such use, are set forth in U.S.

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Patents 3,035,054, 3,035,056, 3,035,057, 3,150,132, and 3,221,014, and in the application for Letters Patent Ser. No. 221,307 filed Sept. 4, 1962 and assigned to the same assignee of the present invention, all of which are discussed more fully hereinafter.

With the utilization of the above described polychlorocyanurates, there remains the problem that bleaches containing polychlorocyanurates cause a substantial loss of textile tensile strength, print color fading, and/or "yellowing" of "white" fabrics. The above described problem is particularly acute in the field of bleaching "treated" textiles.

In the case of treated textiles, it is well known that in recent years there have been made available a wide variety of textile materials which are crease-proofed with the aid of synthetic polymeric materials. The textiles are impregnated or otherwise "treated" (hereinafter used in the same connotation) with these resinous materials usually in an amount of from about 0.25% to about 10% by weight of said resinous material based on the total weight of the textiles. In many cases, the resulting textiles are washable, and such textiles are now quite generally referred to as "wash-and-wear" textiles or fabrics.

The synthetic polymers commonly used for this purpose contain a significant proportion of



groups (e.g. imide or amide groups) in the resin molecule, either in a straight chain or in a cyclic structure. Typical polymers of these types include the polyamides, melamine-formaldehyde resins, open-chain urea-formaldehyde resins and ethylene urea-formaldehyde resins. However with the bleaches heretofore commercially available, these polymers have been so sensitive to reaction with the chlorine-containing or based bleaches that they have been sold with instructions that they are not to be used with such bleaches. The bleaching of textiles treated with these resins thus has presented a serious problem.

After an almost predictable number of washings, a treated fabric, for example, will acquire a yellowish color, and will then develop holes or even disintegrate when subjected to high temperature, as in a dryer or during ironing. Furthermore, there is a substantial reduction in tensile strength of the treated textile. Apparently, the chlorine in the above-described bleaching agent attacks the



groups on the polymer molecule, and converts these to



groups, which are retained during subsequent washings. When



groups of the polymer are heated to a sufficiently high temperature, HCl is liberated which scorches the textile, for example, fabric, attacks the dye, and reduces the tensile strength of the textile. After a sufficient number of



groups have been formed in this way, it is quite easy for the fabric to become severely damaged when heated.

It has been proposed that this problem could be overcome by using polymers containing N-substituted groups, such as the N-substituted cyclic ureas, thus eliminating free



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groups. However, it is very difficult to effect complete replacement of hydrogen in



groups, and cyclization in the cyclic ureas may not be complete. Thus, some NH groups almost invariably remain, which can react with the chlorine-containing bleach to produce



groups. Also, cyclic ureas are sensitive to alkaline hydrolysis, which can take place in the bleaching solution, opening the ring and thus forming NH groups, which then react to form



groups. After about twenty washings, fabrics crease-proofed with polymeric cyclic ureas are no more resistant to the action of chlorine-containing bleach than are open chain urea-formaldehyde resins.

The above described problem can be avoided if non-chlorine-containing bleaches, i.e. oxygen based bleaches, are used or if the bleaching compound is sufficiently unreactive so it does not form



groups. In the latter case, however, the bleaching effect is not as great as is often desired. In the case of oxygen based bleaches, the expense of the bleaching is considerably increased because such bleaches are more expensive, on a performance basis, than the chlorine-containing bleaches.

It has been proposed in U.S. Patent 3,099,625 that the above described problem can be overcome by the utilization of certain organic nitrogenous compounds, generally designated chlorine acceptors, which can be incorporated in a hypochlorite bleaching composition such as sodium, potassium, and calcium hypochlorite. However, surprisingly, the applicant has found that the chlorine acceptors described in this patent do not give satisfactory results when employed with organic chlorine-containing compound, and particularly when used with polychlorocyanurates such as, for example, metal salts of chlorinated cyanuric acids. Furthermore, it was surprising to find, after extensive experimentation hereinafter described, that the above described chlorine acceptors were inadequate to afford substantially complete protection to the treated textiles being bleached. As will be more specifically pointed out in the examples of the present invention, the chlorine acceptors set forth in U.S. Patent 3,099,625 resulted in only partial, i.e. less than 50%, protection, hereinafter more fully explained, to the treated textiles being bleached with (an aqueous solution of) the polychlorocyanurate. Consequently, it was readily ascertainable that this disadvantage of only partial protection must be overcome in order to effectively and commercially utilize the polychlorocyanurates in compositions which are particularly useful in bleaching "treated" textiles.

The aforementioned problems and disadvantages are overcome by practicing the present invention which entails the utilization of the certain bleaching and/or detergent formulations described herein to bleach textiles.

Accordingly, it is one object of the present invention to provide a process which utilizes a bleaching composition which provides substantially complete protection to a treated textile from the deleterious action of said bleach.

Another object of the present invention is to provide bleaching compositions containing an organic nitrogen-containing compound which prevents, when used in an aqueous media, the formation of



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groups on a textile carrying an organic polymer having



groups.

It is a further object of the present invention to provide an improved process for bleaching textiles which have been treated with synthetic polymeric materials which are sometimes classified as "wash-and-wear" textiles.

Further objects and advantages of the present invention will become apparent from the subsequent description and the appended claims.

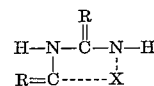
In general, the present invention, in part, provides a process for bleaching a treated textile material which is characterized by containing a polymeric material having in the molecule



groups reactive with a chlorine-containing bleach to form



groups, comprising contacting the textile material with an aqueous solution having a pH less than 11 and a temperature less than 100° C. and consisting essentially of water containing (a) a polychlorocyanurate, hereinafter defined, and (b) an organic nitrogen-containing compound having in one tautomeric form the structural formula



where X is selected from the group consisting of



and



where R is selected from the group consisting of oxygen and NH, and R' is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 10 carbon atoms, until said material is bleached and/or is characterized by having an improved color such as improved whiteness and brilliance. The present invention also provides novel compositions directed to combinations of the above items (a) and (b) alone or with other ingredients, hereinafter described.

The practice of this invention provides an effective way to protect any natural and/or synthetic fibrous base material which is sensitive to chlorination or oxidation due to presence in or on the surface thereof an



group containing cured or water insoluble resinous material for the purpose of crease proofing, or other effects. Typical fibrous base materials of which the textiles may be formed in whole or in part and which are subsequently treated with such resinous or polymeric materials are cotton, nylon, viscose rayon, Dacron, polyester, hemp, linen, jute, and blends thereof such as, for example, cotton-Dacron, cotton-Dacron-viscose rayon, cotton-nylon-viscose rayon, cotton-Dacron-nylon and cotton-nylon (all in various weight ratios). These fibrous base materials are the most commonly used and are the preferred base materials in the treated textiles employed in this invention.

The base materials are treated or impregnated with resinous materials containing



groups to provide the "treated textiles" which are bleached in accordance with the processes of this invention. As examples of such resinous materials there may be mentioned

urea-formaldehyde resins, melamine-formaldehyde resins, triazine-formaldehyde resins, pyrimidone-formaldehyde resins, ethylene urea-formaldehyde resins, guanidine-formaldehyde resins, sulfonamide-formaldehyde resins, triazone-formaldehyde resins, dicyandiamide-formaldehyde and carbamate-formaldehyde resins and the like.

The treated textile materials can be treated in any form, for example, woven and unwoven, as bats, felts, fibers, yarn, roving, silver, and fabrics of all sorts. All of the afore-mentioned fibrous materials, in whatever form they may be, are referred to collectively herein as "textiles."

The polychlorocyanurates employed are characterized by the fact that they contain a metal cation in the molecular structure along with at least one isocyanurate or cyanurate ring and at least two chlorine atoms which provide the source of available chlorine in the bleaching composition used in the novel processes of the present invention. As examples of a particularly suitable group of polychlorocyanurates which may be employed in the novel processes of the present invention, there may be mentioned the following compounds:

- (1) sodium dichloroisocyanurate and hydrates thereof;
- (2) potassium dichloroisocyanurate and hydrates thereof;
- (3) [(monotrichloro)(monopotassium dichloro)] di-isocyanurate
- (4) [(monotrichloro) tetra-(monopotassium dichloro)] pentaisocyanurate;
- (5) magnesium di(dichloroisocyanurate) and hydrates thereof;
- (6) calcium di(dichloroisocyanurate) and hydrates thereof;
- (7) mono-magnesium, di-potassium tetra(dichlorocyanurate) and hydrates thereof;
- (8) mono-zinc, di-potassium tetra-(dichlorocyanurate) and hydrates thereof;
- (9) mono-magnesium, di-rubidium tetra(dichlorocyanurate) and hydrates thereof; and
- (10) mono-zinc, di-rubidium tetra(dichlorocyanurate) and hydrates thereof.

It is also within the scope of the present invention that mixtures of the aforementioned compounds may be used in the formulations if one so desires.

The above compounds, i.e. the polychlorocyanurates and processes for producing the same are disclosed in U.S. Patents Nos. 3,035,054, 3,035,056, and 3,035,057 (as to compounds numbered 1 and 2); 3,150,132 (as to compounds numbered 3 and 4); 3,221,014 (as to compound numbered 5); and 3,072,654 (as to compound numbered 6). The compounds numbered 7-10 and processes for producing the same are disclosed in application for Letters Patent Ser. No. 221,307 filed Sept. 4, 1962, which application is assigned to the same assignee as the present application. In order to avoid the enlargement of this specification, the above patents and patent application should be considered as incorporated herein by reference.

The term "available chlorine" as employed herein is used in its usual technical meaning as employed in the sodium hypochlorite art. The "available chlorine" in a given compound is determined by analyzing for the amount of chlorine that can be liberated from the compound by treatment with an aqueous acid solution.

The metal cation which is present in the molecular structure of the aforementioned polychlorocyanurates is preferably one of the metals of Groups I-A, II-A, and II-B of the Periodic Table of the Elements and includes such metals as lithium, sodium, potassium, rubidium, cesium, francium, barium, strontium, calcium, magnesium, and zinc.

It will be noted throughout the present specification that various chemical terms are used interchangeably, specifically those relating to the polychlorocyanurates. For example, the compounds "sodium dichloroisocyanurate" and "sodium dichlorocyanurate" are the same compounds but connote different tautomeric forms thereof. Conse-

quently, both of these chemical terms are intended to mean the same compound and are used interchangeably herein.

The organic (nitrogenous) compounds employed with the polychlorocyanurates in the novel processes of the present invention, fall within the scope of the Formula I set forth in the earlier part of the description of this invention. These compounds have at least one



group in the molecule and the hydrogen atom on the nitrogen atom is labile and readily replaced by chlorine. In this regard their activity is quite different from the chlorine acceptor compounds disclosed in U.S. Patent No. 3,099,625. As examples of the compounds which come within the aforementioned Formula I when X is a



group, there may be mentioned cyanuric acid, monoalkyl cyanurates, ammelide, alkyl ammelides, ammeline, and alkyl ammelines. Examples of the compounds which fall within said formula when X is a



group include diketo triazines, diamino triazines, and aminoketo-triazines.

However, it has presently been found that cyanuric acid is more desirable and effective for most purposes than the other organic compounds referred to above and hence, cyanuric acid is definitely preferred. However, it is to be understood that organic compounds having in one tautomeric form the structural Formula I given above fall within the scope of the present invention.

It was unexpected to find that the nitrogen-containing compounds falling within the above structural Formula I (and which are disclosed in U.S. Patent No. 3,099,625) gave satisfactory results in the compositions and processes of the present invention whereas the chlorine acceptors disclosed in U.S. Patent 3,099,625, do not give satisfactory results when employed in combination with polychlorocyanurates on an equivalent basis. This difference in effectiveness is more specifically pointed out hereinafter.

It should be noted that the organic nitrogenous compounds utilized in the present invention are all six membered rings wherein there are always two C=R groups, where R is oxygen or NH. Furthermore, there is always present one



group when the



group is substituted in the formula, and one



group when the



group is substituted therein, where R and R' have the significance or meaning hereinbefore defined.

These compounds have shown a unique effectiveness in preventing chlorine damage to "treated" textiles when utilized with the aforementioned polychlorocyanurates. The exact mechanism of protection or prevention is not known. However, in the case of treated textiles it is believed that the chlorine of the hereinbefore described

polychlorocyanurates reacts with or is accepted preferentially by the



groups on the hereinbefore referred to nitrogenous compounds to form



groups and thus there is essentially no chlorine available to react with the less reactive



groups incorporated on the surface of the treated textiles. Thus the last mentioned



groups react only to a negligible extent, if at all, with chlorine in each bleaching cycle. Although it is not intended to limit this invention to the above theory, it appears that the chlorine acceptors described in U.S. Patent No. 3,099,625, do not perform this function in the same manner or in a similar way but, on the contrary, permit a higher degree of reaction between the chlorine and the



groups on the surface of "treated" textiles.

Since the organic (nitrogenous) compounds employed in the present invention are present throughout the bleaching bath, being uniformly dispersed or dissolved therein, their



groups are of course more available for reaction with the bleach than are the resin



groups on or in the "treated" textiles. However, it is likely that only the molecules of such nitrogenous compound in the immediate vicinity of the textile should be considered as taking part in the competitive reaction with the polychlorocyanurate bleach, vis-a-vis the



groups in or on the textile. In this competitive reaction it appears that the resinous



groups in or on the textile are so weak as to retain very little, if any, chlorine. Thus, when the textile is subsequently heated, e.g., during drying, no deleterious amounts of chlorine or HCl are released to tender or weaken the textile. Whatever the mechanism, the result is substantially complete protection of the treated textile (containing resinous



groups) from the deleterious action of the chlorine of the polychlorocyanurate bleach.

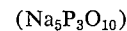
The applicant does not wish to be limited to any theory or ideas presented herein in connection with the operation of his novel bleaching processes.

The quantity of the hereinbefore described organic (nitrogenous) compounds, which are present in the bleaching bath, used in the novel processes of the present invention are dependent to some extent on the amount of the polychlorocyanurate present in said composition. Specifically, the mol ratio of such nitrogen-containing compound to the polychlorocyanurate is usually from about 0.5:1 to about 6:1 and preferably from about 1.5:1 to about 4:1, but under certain conditions it may be possible to use somewhat higher or lower ratios. Stated differently, the compositions of this invention will usually contain from about 0.5 to about 6 mols of the organic nitrogenous

(or nitrogen-containing) compound, e.g., cyanuric acid, per one mol of the polychlorocyanurate.

Although the compositions which are used in the novel processes of the present invention may comprise only the organic nitrogenous compound and a polychlorocyanurate to form a bleaching agent per se, the compositions may also contain a wide variety of inorganic and/or organic compounds to provide detergent formulations which are effective for use in bleaching, sterilizing, oxidizing and/or disinfecting operations.

Examples of inorganic compounds which may be employed in such formulations or compositions include alkaline, water-soluble, alkali metal inorganic salts, preferably those alkaline inorganic salts of this class which are employed as detergent builders. Illustrative of such salts are trialkali metal phosphates such as trisodium phosphate and tripotassium phosphate; di-alkali metal hydrogen phosphates such as di-sodium hydrogen phosphate and dipotassium hydrogen phosphate; alkaline, water-soluble, molecularly dehydrated alkali metal phosphate salts such as alkali metal pyrophosphates, for example, tetra sodium pyrophosphate, trisodium hydrogen pyrophosphate and tetrapotassium pyrophosphate, and the alkali metal triphosphates such as sodium tripolyphosphate



and potassium tripolyphosphate; alkaline, water-soluble alkali metal metaphosphates such as sodium hexameta-phosphate; water-soluble, alkali metal silicates such as sodium silicates having an  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  mol ratio of 1:1 to 1:3.6, preferably 1:1 to 1:1.35, and the corresponding potassium silicates; water-soluble, alkali metal borates such as calcined sodium tetraborate or borax; water-soluble alkali metal carbonates or bicarbonates such as sodium or potassium carbonates or bicarbonates; and the like. These salts can 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 inert neutral alkali metal salt diluents such as neutral alkali metal sulfates or chlorides, for example, sodium sulfate or sodium chloride.

The proportions of the aforementioned alkaline or neutral salts which may be employed in the compositions of this invention can be varied considerably, depending upon the end use of the formulation or composition. However, when used, such salts comprise in excess of about 40% and up to about 90% by weight of the dry solids content of the composition. Of this, the alkaline alkali metal salts usually comprise about 10% to 95% of the total salts and the inert diluent neutral salts usually comprise about 90% to about 5% of the total salts.

Although the compositions of this invention may comprise the above described bleaching agent per se, the compositions may also contain, alone or in combination with the above-described salts, relatively minor amounts usually less than 15% by weight, preferably 1 to 10% by weight, on a solid basis, of perfume or odor masking agent such as essential oils, organic sequestering or chelating agents such as the metal salts of ethylenediamine tetra-acetic acid; organic dyes and coloring agents such as those described in Venkataraman, "Chemistry of Synthetic Dyes," Academic Press, Inc., New York, 1952; organic stain, corrosion, or tarnish inhibitors such as those described in U.S. Patents 2,618,603, 2,618,605, 2,618,606, 2,618,607 and 2,618,608, surface active agents such as foaming agents, detergents, emulsifiers and the like; and mixtures thereof.

In this latter category of surface active agents, particularly nonsoap synthetic organic detergents, there can be included the anionic surfactants, such as the sulfated and the sulfonated alkyl, aryl, and alkylaryl hydrocarbons set forth in U.S. Patent 2,846,398, line 54 of column 3 to line 6 of column 5. There can also be included non-ionic surfactants such as those set forth in column 5 of U.S. Patent 2,846,398 and well-known cationic surfactants.

The portion of U.S. Patent 2,846,398 relating to cer-

tain preferred organic surface active agents which have been found to be particularly advantageous in the compositions of this invention appears in column 4, lines 35 to 75 and column 5, lines 1 to 74, and is quoted below.

"The organic anionic detergents of this invention include in addition to the preferred alkali metal fatty acid soaps the well-known surface active alkali metal sulfonates and sulfates, which may be employed as the sole detergent base or in admixture with the alkali metal fatty acid soaps (e.g. one part of the fatty acid soap to 0.5 to 2 parts by weight of the surface-active alkali metal sulfonate or sulfate or mixture thereof) as the detergent base. A preferred group of this class is the long chain alkyl aryl sulfonates, i.e. those wherein the alkyl radical is straight or branched in structure and contains from 8 to 22 carbon atoms, but preferably 10 to 16 carbon atoms, examples of which being octyl, decyl, dodecyl, keryl, pentadecyl, hexadecyl, octadecyl, mixed long chain alkyls derived from long chain fatty materials such as the lauryl radical, cracked paraffin wax olefins, polymers of lower mono-olefins such as propylene tetramer and the like, and wherein the aryl radical is derived from benzene, toluene, xylene, phenol, the cresols, naphthalene, and the like. Specific examples of such comprise sodium decyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium lauryl benzene sulfonate and sodium hexadecyl benzene sulfonate.

"Other sulfonate surface-active agents are contemplated also, e.g. the long chain alkyl sulfonates such as sodium hexadecane sulfonate and sodium octadecane sulfonate.

"The well-known sulfate detergents having 12 to 26 carbon atoms and particularly those having an acyl radical of about 8 to 22 carbon atoms may be employed as anionic detergent bases in accordance with this invention. Such detergents include the sulfuric acid esters of polyhydric alcohols incompletely esterified with fatty acid, e.g. sodium coconut oil monoglyceride monosulfate, sodium tallow diglyceride monosulfate, the pure and mixed higher alkyl sulfates such as sodium lauryl sulfate and sodium cetyl sulfate.

"Additional anionic surface-active sulfonates and sulfates contemplated by this invention are the sulfated and sulfonated alkyl acid amides such as Igepon T

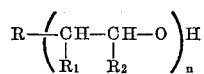


the sulfated and sulfonated esters such as Igepon AP ( $RCOOC_2H_5SO_3Na$  where R is an alkyl radical containing from 12 to 18 carbon atoms), sodium salt of the bisulfate of a dialkyl dicarboxylate, sodium salt of the sulfonic acid derivative of a dialkyl dicarboxylate, sodium sulfosuccinic esters such as



and the like.

"The nonionic surface-active agents contemplated are viscous liquid to wax-like water-soluble surface-active substances containing a polyglycol ether group of the structure



wherein  $R_1$  and  $R_2$  are hydrogen or short chain alkyl, where  $n$  is an integer greater than 3, and where R is a residue of a compound of a monomeric organic compound having an active hydrogen, e.g. alcohols, phenols, amides, primary amines, secondary amines, carboxylic acids, etc. These nonionic detergents are well known (note U.S. 1,970,578 and U.S. 2,213,477) and may be typified by the polyalkylene oxide derivatives (i.e. polyethylene oxide, polypropylene oxide, polybutylene oxide) of water-insoluble higher fatty acids, such as lauric, oleic, palmitic and stearic acid and the like or mixtures thereof, such as the mixtures of fatty acids obtained from animal and vegetable fats and oils or by oxidation of

petroleum fractions such as paraffin wax. They may also be exemplified by the polyalkylene oxide derivatives of such water-insoluble organic hydroxy compounds as higher aliphatic alcohols (i.e. the alcohols corresponding to the fatty acids specified above or mixtures thereof), oil or phenols, particularly alkyl phenols containing at least six alkyl carbon atoms such as isooctyl-, di-tertiary butyl-, triisopropyl-, nonyl, dodecyl-, octadecyl-phenols or naphthols, or of higher alkyl alcohols, such as benzyl alcohol, cinnamyl alcohol. They may also be exemplified by the polyalkylene oxide derivatives of such amines as stearyl, lauryl, dicyclohexyl, dibutyl amine and the like. A particularly useful nonionic detergent is that obtained by condensing one mol of tall oil with 5 to 15 mols of ethylene oxide."

Other typical examples of these categories of the anionic and nonionic surface active agents are described in Schwartz and Perry, "Surface Active Agents," Interscience Publishers, New York (1949) and "The Journal of American Oil Chemists Society," vol. 34, No. 4, pp. 170-216 (April 1957). In order to avoid the enlargement of the present specification, the subject matter of all the aforementioned publications including the aforementioned patents, i.e. 2,618,603, 2,618,605, 2,618,606, 2,618,607, 2,618,608 and 2,846,398, is incorporated herein by reference.

The various ingredients referred to herein can be used in the compositions or formulations in various proportions depending on whether the composition is to be used as a bleaching composition, a disinfecting composition, a dishwashing composition, etc. However and as a preferred embodiment herein, the present invention is generally directed toward using the various ingredients in certain amounts to form a bleaching composition for use in bleaching "treated" textiles.

In a preferred embodiment of the invention, the bleaching composition comprises (a) a polychlorocyanurate, which has at least one metal cation in its molecular structure, selected from the group consisting of

sodium dichloroisocyanurate and hydrates thereof;  
potassium dichloroisocyanurate and hydrates thereof;  
[(monotrichloro)(monopotassium dichloro)] di-isocyanurate;  
[(monotrichloro) tetra-(monopotassium dichloro)] pentaisocyanurate;  
magnesium di(dichloroisocyanurate) and hydrates thereof;  
calcium di(dichloroisocyanurate) and hydrates thereof;  
mono-magnesium, di-potassium tetra(dichlorocyanurate) and hydrates thereof;  
mono-zinc, dipotassium tetra-(dichlorocyanurate) and hydrates thereof;  
mono-magnesium, di-rubidium tetra(dichlorocyanurate) and hydrates thereof;  
monozinc, di-rubidium tetra(dichlorocyanurate) and hydrates thereof; and

mixtures thereof; (b) cyanuric acid; and (c) a detergent builder salt selected from the group consisting of neutral and alkaline, alkali metal phosphates, alkali metal silicates having an alkali metal oxide to silica mol ratio of 1:1 to 1:3.6, alkali metal sulfates, alkali metal borates, alkali metal carbonates, alkali metal bicarbonates, and mixtures thereof. In addition to the various ingredients (a), (b), and (c) listed above or in place of the detergent builder salt, (c), there may be utilized a nonsoap synthetic organic detergent selected from the group consisting of nonsoap synthetic nonionic surface active agents and nonsoap synthetic anionic surface active agents.

In another preferred embodiment of the invention, a sterilizing, disinfecting, bleaching, or sanitizing composition comprises an intimate mixture of (a) a polychlorocyanurate which has at least one metal cation in its molecular structure, (b) cyanuric acid, (c) a detergent

builder salt, and (d) a nonsoap synthetic organic detergent, the total amount by weight of the combination of (a), (b) and (d) being less than the amount of (c).

In still another preferred embodiment of the present invention, there is a bleaching composition comprising an intimate, dry mixture of (a) from about 0.05% to about 10% by weight, based on the weight of the composition, of potassium dichloroisocyanurate or [(monotrichloro) tetra-(monopotassium dichloro)] pentaisocyanurate; (b) from about 1.5 to about 4 mols, per mol of said potassium dichloroisocyanurate or pentaisocyanurate, of cyanuric acid; (c) from about 40% to about 90% by weight, based on the weight of the composition, of a mixture of sodium tripolyphosphate, sodium sulfate, sodium metasilicate, and potassium silicate; and (d) from about 1% to about 10% by weight, based on the weight of the composition, of sodium dodecylbenzene sulfonate.

In most instances, the proportion and kind of ingredients in the formulations employed 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.

The compositions used in the novel processes of this invention can be prepared in a variety of ways. Thus the ingredients can be and preferably are mixed as solid particles to provide a mixture, preferably a uniform mixture, of solid particles, usually in the form of a free-flowing mixture. However, the ingredients can be mixed as solid particles and then briquetted or tableted or otherwise compressed in the form of cakes, cubes, etc. The ingredients can also be dissolved or slurried in water and sold as aqueous slurries or solutions, or these can be dried, for example, by drum drying to obtain flakes which can be used as such or ground to powder form. The aqueous solutions or slurries can also be spray dried in the form of beads or hollow spheres.

The novel processes of utilizing the above-described formulations in the present invention are carried out, in general, by contacting the hereinbefore defined "treated" textile materials with an aqueous solution containing the aforementioned bleaching and/or detergent formulations dissolved and/or suspended therein. Specifically, it is preferred that the aqueous treating solution or suspension employed have a pH in the range of from about 0.25 to about 10.5. In the case of neutral or alkaline solutions or suspensions, the pH thereof is usually within the range of 6.5 to about 9.5. The temperature of the aqueous treating solutions heretofore defined is preferably in the range of from about 5° C. to about 75° C.

The amount of the above-described bleaching and/or detergent formulations which are employed with water to form the aqueous treating solution or suspension will vary to some extent depending upon the amount of bleaching which it is desired to impart to the various textile materials. For most purposes, however, the use of the bleaching and detergent compositions in an amount sufficient to provide from about 0.01% (i.e. 100 p.p.m.) to about 8% of available chlorine, based on the weight of the aqueous solution containing said composition, is adequate.

In a preferred embodiment of the present invention there is provided a process for bleaching treated textile materials having a base material from the group cotton, nylon, viscose rayon, dacron, hemp, linen, jute and blends thereof, such as cotton-Dacron, cotton-Dacron-viscose rayon, cotton-nylon-viscose rayon, cotton-Dacron-nylon and cotton-nylon, and containing in or on the base material a water-insoluble polymeric material having in the molecule



groups which tend to react with a chlorine-containing bleach to form N—Cl groups by subjecting such textile material to the bleaching action of an aqueous solution consisting essentially of water containing (1) a polychlo-

rocyanurate having at least one alkali metal cation within its molecular structure, (2) cyanuric acid, (3) a detergent builder salt, and (4) a nonsoap synthetic organic detergent, the total amount of (1), (2), and (4) being less than the amount of (3), the relative amounts of such ingredients used being sufficient to inhibit the formation, by the chlorine of the polychlorocyanurate, of N—Cl groups on the polymer molecule and with the proviso that the aqueous bleaching solution have a pH of from about 0.25 to about 10.5 and a temperature of from about 5° C. to about 75° C. By so proceeding, it is possible to effectively bleach such textile materials without materially reducing the tensile strength thereof.

In another preferred embodiment of the present invention, there is provided a process for bleaching a cotton fabric containing in or on the surface thereof a cured or water-insoluble urea-formaldehyde or ethylene urea-formaldehyde polymeric material having in the molecule



groups which tend to react with a chlorine-containing bleach to form



groups, by subjecting such cotton textile material to the bleaching action for a period of about 5–15 minutes of an aqueous solution having a temperature of about 10 to about 65° C. and a pH of about 6.5 to about 9.5 and consisting essentially of water and a composition comprising (a) from about 0.05% to about 10.0% by weight, based on the weight of the composition, of potassium dichloroisocyanurate or [(monotrichloro) tetra-(monopotassium dichloro)] pentaisocyanurate; (b) from about 1.5 to about 4 mols, per mol of said potassium dichloroisocyanurate (or said pentaisocyanurate), of cyanuric acid; (c) from about 40% to about 90% by weight, based on the weight of the composition, of a mixture of sodium tripolyphosphate, sodium sulfate, sodium metasilicate, and sodium (or potassium) silicate; and (d) from about 1% to about 10% by weight, based on the weight of the composition, of sodium alkyl benzene sulfonate in which the alkyl group is a linear chain of about 10 to about 15 carbon atoms. The composition is employed in an amount sufficient to provide a concentration of at least 50 parts, preferably 100–500 parts, of available chlorine per one million parts of said solution and thus inhibits the formation of



groups on the cured polymer molecule. The practice of such process substantially inhibits or prevents the textile tensile strength loss of the treated cotton fabric.

A further understanding of the novel processes and compositions of this 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 indicated.

#### EXAMPLE I

A series of experiments were conducted on a "treated" textile material in order to demonstrate the improved "brightening" or "whiteness" resulting from the utilization of the bleaching agents or compositions in the novel processes of the present invention. The bleaching agents set forth in Table I were mixed together immediately prior to bleaching by weighing the individual solid ingredients separately and then mixing them together in a dry state. These dry mixed bleaching agents were individually dissolved in one liter of water contained in a Terg-O-Tometer (U.S. Testing Company, Inc.) which is a standard testing device used in the detergent art for conducting such bleaching tests. The amount of each bleaching agent used was sufficient to provide the chlorine or oxygen concentrations listed in Table I. In addition to the dry mixed

compositions, there was added to each liter of water approximately 0.05% by weight, based on the weight of said compositions, of a surfactant such as sodium alkyl benzene sulfonate in which the alkyl group is a linear chain of about 10 to about 15 carbon atoms and which is com-

prior art compositions. The use of sodium perborate as a bleach is exemplified in order to illustrate relative  $\Delta R_d$  obtained using an oxygen-based bleach and to show the more effective bleaching obtained by a chlorine-based bleach as contrasted to an oxygen-based bleach.

TABLE I

Bleach <sup>1</sup>	Nitrogen Compound	Mol Ratio <sup>2</sup>	Chlorine or O <sub>2</sub> Concentration, p.p.m.	Washing Solution pH	$\Delta R_d$ <sup>3</sup> of Textile <sup>4</sup>
Sodium Dichlorocyanurate.....	Cyanuric Acid.....	0.5:1	200	7.5	8.71
Do.....	do.....	2:1	200	7.5	6.77
Do.....	do.....	4:1	200	7.5	5.76
Do.....	do.....	4:1	100	7.5	4.88
Do.....	do.....	4:1	50	7.5	4.14
Do.....	Melamine <sup>5</sup> .....	4:1	200	7.5	2.52
Do.....	Dimethyl Hydantoin <sup>5</sup> .....	4:1	200	7.5	3.74
Do.....	Urea <sup>6</sup> .....	4:1	200	7.5	2.21
Do.....	.....	.....	200	7.5	1.48
Sodium Perborate.....	.....	.....	<sup>a</sup> 45.2	9.3	1.64
Do.....	.....	.....	<sup>a</sup> 22.6	9.3	0.93
Do.....	.....	.....	<sup>a</sup> 11.3	9.3	0.62
Trichlorocyanuric Acid.....	Cyanuric Acid.....	4:1	200	7.5	3.98

<sup>1</sup> Compound used to supply either available chlorine or oxygen for bleaching purposes.

<sup>2</sup> Mol ratio of nitrogen compound to bleach compound.

<sup>3</sup> Measurement of total light reflectance; the larger value indicates a more effective bleaching without "yellowing" of the fabric or deterioration thereof.

<sup>4</sup> Unbleached cotton sheeting (muslin) treated with urea-formaldehyde resin.

<sup>5</sup> Chlorine acceptors as exemplified in U.S. Patent 3,099,625.

<sup>6</sup> O<sub>2</sub> concentration.

mercially available under the registered trademark Santomerse. The pH of the aqueous bleaching solution was then adjusted with either NaOH or HPO<sub>3</sub> to the pH values listed in Table I.

To each of the aqueous bleaching agents or compositions prepared in the Terg-O-Tometer, there was then added a 5" x 5" piece or swatch of unbleached cotton muslin which was not soiled but which had a natural grayish color and which had been previously treated with a urea-formaldehyde resin (cured to the water-insoluble state) in order to provide



groups on the surface of said muslin. (Specifically the muslin material was crease-proofed with a methylated urea-formaldehyde resin. The muslin was padded with an aqueous bath of 7.5% methylated urea-formaldehyde resin and 0.86% magnesium chloride hexahydrate. The resin was applied in a laboratory type padder, with one dip and one nip, at a 79% wet pick up. The muslin was then frame dried and cured in one operation at 305° F. for twelve minutes.) In addition, there was also added to the bleaching solutions a sufficient amount of clean, white (unstained) fill cloth to give an aqueous solution:cotton cloth weight ratio of 20:1. The Terg-O-Tometer was then set for a rate of agitation of 100 cycles per minute and each cotton swatch was given a single 10-minute washing at 140° F. The cotton muslin swatch was then removed from the Terg-O-Tometer, air dried at about 70° C., pressed, and then subjected to a total light reflectance test in order to compute the difference in reflectance before and after washing, i.e., to determine the increase in brightening of the swatches due to bleaching. This reflectance test was carried out with the use of a Model D-1 Color-Eye, Instrument Development Laboratories, Inc., and the values obtained, designated as  $\Delta R_d$ , are set forth in Table I. (The reflectance of both sides of each swatch was determined at least five times in order to attain a representative reading. The  $\Delta R_d$ , then, is the difference of these averages.)

It will be noted that of the nitrogen compounds listed in Table I, melamine, dimethyl hydantoin, and urea were of the prior art chlorine acceptors set forth and exemplified in U.S. Patent 3,099,625. When these acceptors are used with polychlorocyanurates, it has been found that the loss in tensile strength is 50% to as high as 400% greater than with cyanuric acid of the present invention. Since even relatively small losses in tensile strength are undesirable from a consumer viewpoint, it can readily be seen then that the use of cyanuric acid of the present invention is a significant improvement as contrasted to the

The bleaching effect obtained by using a mixture of trichlorocyanuric acid and cyanuric acid is illustrated at the end of Table I. It should be noted that trichlorocyanuric acid does not contain any metal cations in its molecule and, therefore, is not a polychlorocyanurate as defined in the present specification. The bleaching effect of trichlorocyanuric acid was included in Table I in order to compare it with the bleaching effect obtained by the use of a polychlorocyanurate in accordance with the processes of the present invention. On a comparative testing basis (at the same level of available chlorine), the sodium dichlorocyanurate-cyanuric acid mixture subsequently yielded a processed muslin which has a  $\Delta R_d$  of 5.76 compared to the value of 3.98 which was obtained by processing another similar piece of muslin with the trichlorocyanuric acid-cyanuric acid mixture. While cyanuric acid has in the past been suggested for use in compositions which contain trichlorocyanuric acid (note U.S. Patents 2,980,622 and 3,213,029), it can readily be seen, then, that there is a significant improvement and unexpected result over such trichlorocyanuric compositions when cyanuric acid is used with the herein defined polychlorocyanurate in the novel processes of the present invention.

#### EXAMPLE II

A second series of experiments were conducted on a commercially available "wash-and-wear" white cotton fabric which had been treated with a methylated melamine-formaldehyde resinous material (cured and water-insoluble) having



groups thereon by the "treating" procedure set forth in the second paragraph of Example I. The purpose of this series of tests was to determine the textile tensile strength loss, if any, between an air dried fabric and a fabric which has been subjected to heat treatment (to simulate ironing) after 5 and 10 machine washes when utilizing the bleaching compositions in the novel processes of the present invention. The bleaching compositions set forth in Table II were prepared immediately prior to the washing by weighing the individual solid ingredients separately and then mixing them together in the dry state. A Kenmore® washing machine having a 17-gallon capacity was then completely filled with water having a temperature of 140° F. The dry mixed bleaching composition was then dissolved in the aforementioned quantity of water. Added to this bleaching solution was approximately 0.05% by weight, based on the weight of said dry mixed

bleaching composition, of a surfactant such as sodium alkyl benzene sulfonate in which the alkyl group is a linear chain of about 10 to about 15 carbon atoms and which is commercially available under the registered trademark Santomerse. The overall pH of the aqueous bleaching solution was then adjusted with NaOH or HPO<sub>3</sub> to a pH of approximately 7.5. The amount of bleaching composition added to the water was sufficient to provide a bleaching solution containing approximately 200 p.p.m. of available chlorine. Next, there was added to the bleaching solution duplicate 18" x 18" pieces of the aforementioned wash-and-wear white cotton fabric and also sufficient amount of (unstained) fill cloth in order to give a wash load of approximately 6 lbs.

The washing machine was then operated under normal conditions; one of the duplicate test samples of wash-and-wear cotton fabric was removed after 5 washes and the other sample was removed after 10 wash cycles and both were air dried at approximately 70° F. Each sample was then cut in two half pieces and one of the half pieces was subjected to heat treatment by contacting both faces of said half piece with two parallel plates (one plate per face or side) which were maintained at a temperature of 365° F.<sup>±2</sup> for approximately 30 seconds. The tensile strength of each half sample of the 18" x 18" white cotton fabric was then determined by using an Instron Tester. The procedure set forth above is the same as that specified in the American Association of Textile Chemists and Color Standard Method No. 92-1962 which relates to the test for fabric damage due to chlorine pick up.

The values obtained from the measurements of the tensile strength of the various samples bleached by the aforementioned procedure are disclosed in Table II. It will be noted that the values set forth under the columns designated "unscorched" were the values obtained on the half samples which were not subjected to any heat treatment (i.e. air dried only) wherein the values set forth under the columns headed "scorched" were obtained on the samples which were subjected to the aforementioned heat treatment, which promotes the liberation of HCl which, in essence, "scorches" the material. Such heat treatment is similar to those conditions which the fabric would be subjected to if it were "ironed" by the consumer.

As can readily be seen from Table II, the utilization of a bleach such as sodium dichlorocyanurate per se results in a significant loss in tensile strength both after 5 and 10 washes whereas the combination therewith on one of the organic nitrogenous compounds of the present invention, such as ammeline or cyanuric acid, substantially inhibited loss in tensile strength. A prior art compound, dimethyl hydantoin, exemplified in U.S. Patent 3,099,625, was also utilized with the aforementioned sodium dichlorocyanurate. Table II discloses the results obtained when using such prior art compound of the class disclosed in such patent, and more specifically discloses that a substantial loss of tensile strength of the treated textile results from such combination as compared to only a slight loss of tensile strength of the treated textile which results when using the organic nitrogenous compound of the present invention.

## EXAMPLE III

The following example demonstrates the effect on textile color fading when using the compositions of the present invention and others known in the art.

The washing procedure as set forth in Example II was repeated utilizing (commercially available "treated") fabrics designated A, B, and C, as defined in Table III. A bleaching composition containing either sodium dichlorocyanurate per se or sodium dichlorocyanurate plus cyanuric acid in different mol ratios was utilized in a sufficient amount in order to yield a bleaching solution containing approximately 200 p.p.m. available chlorine and having a pH of 7.8 which was adjusted with the addition of NaOH or HPO<sub>3</sub>. The initial solution temperature was 140° F. The washing machine was operated under normal conditions and the test samples were then removed after 1, 5, and 10 washes and subsequently air dried. These test samples were then visually observed for relative color change, the results of which are set forth in Table III. The results of this series of experiments vividly demonstrate the significant improvement in avoiding of color fading which was obtained when using the bleaching formulations in the novel processes of the present invention. These formulations include the nitrogenous compounds heretofore described and are contrasted to results obtained by the utilization of an alkali metal salt of a chlorinated cyanuric acid per se.

TABLE III.—TEXTILE FADING TEST<sup>1</sup>

Mol Ratio <sup>2</sup> .....	Bleach		
	Sodium Dichlorocyanurate	Sodium Dichlorocyanurate	Sodium Dichlorocyanurate
	Nitrogen Compound		
	None	Cyanuric Acid	Cyanuric Acid
	None	2:1	4:1
After One Wash Cycle			
Fabric No.: <sup>3</sup>			
A.....	90	20	10
B.....	20	10	10
C.....	8	3	3
After Five Wash Cycles			
A.....	100	90	70
B.....	60	25	12
C.....	10	5	5
After Ten Wash Cycles			
A.....	<sup>4</sup> 100	98	90
B.....	90	50	25
C.....	20	10	7

<sup>1</sup> The color component that changed the most, which was assigned an arbitrary number of 100, was used as a basis for estimating color changes visually.

<sup>2</sup> Mol ratio of nitrogen compound:bleach.

<sup>3</sup> Fabric No.—A=Ameritex "Playknit," cotton print; colored blue-green, light brown, lilac; crease resistant finish (triazone-formaldehyde resin); preshrunk; and guaranteed washable. B=Shirley Fabric Corporation "Serrano"; 79% viscose rayon and 21% plain cotton; orange; and washable; finished with a melamine-formaldehyde resin. C=Same as A except solid blue color.

<sup>4</sup> Larger number indicates the worst case of color fading.

TABLE II

Bleach <sup>1</sup>	Nitrogen Compound	Mol Ratio <sup>2</sup>	Textile <sup>3</sup> Tensile Strength, lbs.					
			After 5 Washes			After 10 Washes		
			Unscorched <sup>4</sup>	Scorched <sup>5</sup>	Percent Loss	Unscorched <sup>4</sup>	Scorched <sup>5</sup>	Percent Loss
Sodium Dichlorocyanurate.....			56.7	34.3	39.5	50.8	20.8	59.1
Do.....	Cyanuric Acid.....	0.5:1	53.4	42.1	27.9	53.6	38.0	29.1
Do.....	Dimethyl Hydantoin <sup>6</sup> .....	4:1	56.2	35.8	36.1	54.5	27.7	49.2
Do.....	do.....	2:1	55.2	54.1	2.0	55.5	52.4	5.6
Do.....	do.....	4:1	53.5	53.0	0.9	52.3	50.9	2.7
Magnesium di(dichloroisocyanurate).....	Cyanuric Acid.....	4:1	54.3	52.7	2.9	56.8	54.6	3.9
Do.....	Ammeline.....	4:1	57.6	52.9	8.1	55.1	50.0	9.3

<sup>1</sup> Compound used to supply available chlorine, i.e. the metal salt of dichlorocyanuric acid.

<sup>2</sup> Mol ratio of nitrogen compound to bleach compound.

<sup>3</sup> "Wash-and-Wear" white cotton fabric treated with a methylated melamine-formaldehyde resin.

<sup>4</sup> No heat treatment.

<sup>5</sup> Subjected to heat treatment, i.e. 365±2° F, which liberates any HCl present and thus causes fiber deterioration.

<sup>6</sup> Compound as exemplified in U.S. Patent 3,099,625.



## EXAMPLE IV

A series of experiments relating to the loss of fabric tensile strength were conducted in this Example IV in a similar manner as that set of experiments set forth in the above described Example II. This series of experiments of Example IV illustrates the effect of various bleaching compositions on the tensile strength of a "wash-and-wear" white cotton fabric, characterized by having been pretreated with a polymeric resinous material as described in Table IV and which contains —NH— groups on the surface of or in the fabric, when utilizing the present invention bleaching agents, i.e., a polychlorocyanurate and a nitrogen-containing compound, in a detergent formulation. Dry bleaching compositions were prepared containing the various ingredients shown in Table IV, the quantities of each ingredients being expressed in percent by weight. The bleaching compositions designated A through N were then utilized in the same manner as the washing procedure set forth and described in Example II. The fabrics washed in compositions A–N were removed from the washing machine after 10 washes, or heated as the case may be with the other half pieces, air dried, and tested on the Ingstron Testor. The results of this series of experiments are shown in the third from the last horizontally extending column in Table IV and depict the percent loss in tensile strength, i.e. the tensile strength before and after heat treatment, of the fabric after 10 washes with the various bleaches A through N. It can readily be seen from Table IV that the compositions A through L which incorporated a present invention nitrogen-containing compound were far superior to the results obtained from the textile material washed in the compositions M and N which did not include the nitrogen-containing compound. Specifically, the bleaching compositions M and N yielded a percent loss in textile tensile strength on the average of about 61% after 10 washes as contrasted to an average of about 9% loss in tensile strength after 10 washes with the present invention bleaching compositions.

The procedure of Example IV was again repeated utilizing a nylon fabric treated with a urea-formaldehyde

IV and depict the percent loss in tensile strength of the nylon fabric after 10 washes with the various bleaches A through N. It can readily be seen from Table IV that the compositions A through L which incorporate a present invention nitrogen-containing compound were far superior to the results obtained from the nylon textile material washed in the compositions M and N which did not include the nitrogen-containing compound. Specifically, the bleaching compositions M and N yielded a percent loss in nylon textile tensile strength on the average of about 71% after 10 washes as contrasted to an average of about 8–9% loss in tensile strength after 10 washes with the present invention bleaching compositions.

The procedure of Example IV was again repeated utilizing a textile material comprising 60% white cotton fabric and 40% Dacron polyester fabric treated with an ethylene urea-formaldehyde resin (cured and water-insoluble) containing —NH— groups. The results of this procedure are shown in the last horizontally extending column in Table IV. These results are quite similar to the end results obtained utilizing the cotton fabric and the nylon fabric as previously mentioned. Specifically, the bleaching compositions M and N yielded a percent loss in cotton-Dacron textile tensile strength on the average of about 71% after 10 washes as contrasted to an average of about 8.5% loss in tensile strength after 10 washes with bleaching compositions A through L which exemplify the compositions utilized in the novel processes of the present invention.

As can readily be seen from the aforementioned Examples I through IV, the bleaching agents or detergent formulations when used in the novel processes of the present invention significantly protect the "treated" textile material (being subjected to a bleaching solution) from loss of tensile strength from the chlorine contained in the bleaching solution. When contrasted to the prior art detergent formulations such as exemplified in U.S. Patent 3,099,625, the present invention compositions are about 200% to about 600% times more effective in this respect and thus they substantially promote a longer life of the textile fabric which is a highly desired end result from the consumer point of view.

TABLE IV

Ingredients	Bleaching Composition													
	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Bleach: <sup>1</sup>														
1.....	6													6
2.....		6												
3.....			7											
4.....				8										
5.....					5									
6.....						5						6	6	6
7.....							7							
8.....								7						
9.....									7					
10.....										8				
Chlorine Acceptor:														
Cyanuric Acid.....	3	3	3	3	3	3	3	2	3	3		3	3	
Ammeleine.....														
Inorganic Salt:														
Sodium tripolyphosphate.....	40	40	40	40	41	41	39	40	40	40	40	44	43	43
Sodium sulfate.....	27	27	26	25	27	27	27	27	25	25	27	27	27	27
Sodium metasilicate.....	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Potassium silicate.....	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Surfactant, Sodium Dodecylbenzene sulfonate (linear dodecyl chain).....	4	4	4	4	4	4	4	4	4	4	4	4	0	4
Percent Loss in Textile Tensile Strength After 10 Washes:														
Cotton <sup>2</sup> .....	5.7	6.4	8.6	11.1	4.8	5.5	10.1	11.8	8.6	9.3	12.2	14.1	57.7	63.9
Nylon <sup>3</sup> .....	4.8	6.6	5.1	7.4	10.2	8.9	6.1	9.7	8.5	10.2	11.7	13.8	65.1	74.2
Cotton-Dacron <sup>4</sup> .....	6.3	7.5	4.2	8.6	11.7	7.4	9.9	8.4	9.1	12.1	9.3	12.6	71.6	70.8

<sup>1</sup> Bleaches numbers 1–10 correspond respectively to the polychlorocyanurates numbered 1–10 which are set forth on pages 7–8 of the present specification.

<sup>2</sup> "Wash-and-wear" white cotton fabric treated with a triazone-formaldehyde resin by the "treating" procedure set forth in the second paragraph of Example I.

<sup>3</sup> Nylon fabric treated with a urea-formaldehyde resin by the "treating" procedure set forth in the second paragraph of Example I.

<sup>4</sup> A blend of 60% white cotton fabric and 40% Dacron fabric treated with an ethylene urea-formaldehyde resin by the "treating" procedure set forth in the second paragraph of Example I.

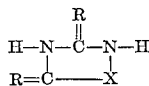
resin (cured and water-insoluble) and having —NH— groups on the surface of the fabric. The procedure set forth was substantially the same as that set forth in Example IV. The results of this procedure are shown in the next to last horizontally extending column in Table

What is claimed is:

1. A sterilizing, disinfecting, bleaching, and sanitizing composition consisting essentially of an intimate mixture of (a) a polychlorocyanurate which has at least one metal cation, selected from the group consisting of alkali metal

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and alkaline metal earth cations in its molecular structure and (b) an organic compound having in one tautomeric form the structural formula



where X is selected from the group consisting of



and



where R is selected from the group consisting of oxygen and NH and R' is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 10 carbon atoms, the ratio of said polychlorocyanurate to said organic compounds being from about 1:0.5 to 1:6.

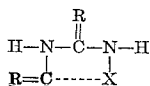
2. The composition as set forth in claim 1 wherein the organic compound is cyanuric acid; the mol ratio of the polychlorocyanurate to the cyanuric acid is from about 1:0.5 to about 1:6; and the composition further includes (a) a detergent builder salt selected from the group consisting of neutral and alkaline, alkali metal phosphates, alkali metal silicates having an alkali metal oxide to silica mol ratio of 1:1 to 1:3.6, alkali metal sulfates, alkali metal borates, alkali metal carbonates, alkali metal bicarbonates, and mixtures thereof and (b) a nonsoap synthetic organic detergent selected from the group consisting of nonsoap synthetic nonionic surface active agents and nonsoap synthetic anionic surface active agents, said composition containing from 0.05% to 10% by weight of said polychlorocyanurate, from 40% to 90% by weight of said builder salt and from 1% to 10% by weight of said detergent.

3. The composition as set forth in claim 2 wherein the said polychlorocyanurate is pentaisocyanurate.

4. The composition as set forth in claim 2 wherein the said polychlorocyanurate is potassium dichloroisocyanurate.

5. A bleaching composition consisting essentially of an intimate, dry mixture of (a) from about 0.05% to about 10.0% by weight, based on the weight of the composition, of a pentaisocyanurate; (b) from about 1.5 to about 4 mols, per mol of said pentaisocyanurate, of cyanuric acid; (c) from about 40% to about 90% by weight, based on the weight of the composition, of a mixture of sodium tripolyphosphate, sodium sulfate, sodium metasilicate, and potassium silicate; and (d) from about 1% to about 10% by weight, based on the weight of the composition, of a sodium alkylbenzene sulfonate having from about 10 to 16 carbon atoms in a linear alkyl chain.

6. In a process for bleaching a treated textile material which is characterized by containing a polymeric material having in the molecule NH groups reactive with a chlorine-containing bleach to form N-Cl groups, wherein said textile material is bleached with a chlorine-containing bleach, the improvement which comprises contacting said textile material with an aqueous solution consisting essentially of water, a polychlorocyanurate which has at least one metal cation selected from the group consisting of alkali metal and alkaline metal earth cations in its molecular structure and an organic nitrogen containing compound having in one tautomeric form the structural formula



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where X is selected from the group consisting of

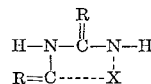


5 and



10 where R is selected from the group consisting of oxygen and NH, and R' is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 10 carbon atoms, until said material is bleached.

7. A process of bleaching a treated textile material which is characterized by containing a polymeric material having in the molecule NH groups reactive with a chlorine-containing bleach to form N-Cl groups, comprising contacting the textile material with an aqueous solution having a pH less than 11 and a temperature less than 100° C. and consisting essentially of water, a polychlorocyanurate which has at least one metal cation selected from the group consisting of alkali metal and alkaline metal earth cations in its molecular structure and an organic nitrogen-containing compound having in one tautomeric form the structural formula



30 where X is selected from the group consisting of



and



40 where R is selected from the group consisting of oxygen and NH, and R' is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 10 carbon atoms, until said material is bleached.

8. The process as set forth in claim 7 wherein the mol ratio of the polychlorocyanurate to the organic compound is from about 1:0.5 to about 1:6 and the organic compound is cyanuric acid.

9. The process as set forth in claim 7 wherein the solution includes a detergent builder salt selected from the group consisting of neutral and alkaline, alkali metal phosphates, alkali metal silicates having an alkali metal oxide to silica mol ratio of 1:1 to 1:3.6, alkali metal sulfates, alkali metal borates, alkali metal carbonates, alkali metal bicarbonates, and mixtures thereof and the organic compound is cyanuric acid.

10. The process as set forth in claim 7 wherein the solution includes a nonsoap synthetic organic detergent selected from the group consisting of nonsoap synthetic nonionic surface active agents and nonsoap synthetic anionic surface active agents and the organic compound is cyanuric acid.

11. The process as set forth in claim 8 wherein the said polychlorocyanurate is pentaisocyanurate.

12. The process as set forth in claim 8 wherein the said polychlorocyanurate is potassium dichloroisocyanurate.

13. The process as set forth in claim 7 wherein (1) the treated textile material is selected from the group consisting of cotton, nylon, viscose rayon, Dacron, hemp, linen, jute, cotton-Dacron, cotton-Dacron-viscose rayon, cotton-nylon-viscose rayon, cotton-Dacron-nylon and cotton-nylon; (2) the said organic compound is cyanuric acid; and (3) the said aqueous solution has a pH of from about 0.25 to about 10.5, a temperature of from about 5° C. to about 75° C. and includes, in addition to the water, said polychlorocyanurate, and cyanuric acid, a detergent builder salt and a nonsoap synthetic organic detergent, the

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total amount by weight of the combination of said polychlorocyanurate, cyanuric acid, and organic detergent being less than the amount of said builder salt.

14. The process as set forth in claim 13 wherein (1) the said polychlorocyanurate is selected from the group consisting of sodium dichloroisocyanurate and hydrates thereof; potassium dichloroisocyanurate and hydrates thereof; di-isocyanurate; pentaisocyanurate; monomagnesium, di-potassium tetra(dichlorocyanurate) and hydrates thereof; mono-zinc, di-potassium tetra-(dichlorocyanurate) and hydrates thereof; and mixtures thereof; (2) the mol ratio of said polychlorocyanurate to cyanuric acid is from about 1:0.5 to about 1:6; (3) the detergent builder salt is a mixture of sodium tripolyphosphate, sodium sulfate, sodium metasilicate and potassium silicate; and (4) the nonsoap synthetic organic detergent is a sodium alkyl benzene sulfonate having from about 8 to about 22 carbon atoms in the alkyl group.

15. A process for bleaching cotton textile materials containing a polymeric material having in the molecule



groups which tend to react with a chlorine-containing bleach to form



groups, said polymeric material being used to pretreat the said cotton textile in an amount of from about 0.25% to about 10% by weight based on the weight of the said cotton textile, comprising subjecting said cotton textile material to the bleaching action of an aqueous solution consisting essentially of water and a composition com-

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prising (a) from about 0.05% to about 10.0% by weight, based on the weight of the composition, of pentaisocyanurate; (b) from about 1.5 to about 4 mols, per mol of said pentaisocyanurate, of cyanuric acid; (c) from about 40% to about 90% by weight, based on the weight of the composition, of a mixture of sodium tripolyphosphate, sodium sulfate, sodium metasilicate, and sodium silicate; and (d) from about 1% to about 10% by weight, based on the weight of the composition, of sodium alkyl benzene sulfonate in which the alkyl group is a linear chain of about 10 to about 15 carbon atoms, said composition being in an amount sufficient to provide a concentration of at least 50 parts of available chlorine per one million parts of said solution and thus substantially inhibit the formation of N-Cl groups on the polymer molecule and consequently substantially reduce the textile tensile strength loss, said aqueous solution having a pH of from about 6.5 to about 9.5, a temperature of from about 10° C. to about 65° C., and being in contact with said textile for a period of from about 5 to about 15 minutes.

## References Cited

## UNITED STATES PATENTS

25	3,150,132	9/1964	Symes.	
	3,294,690	12/1966	Matzner	252-99
	3,336,228	8/1967	Fuchs et al.	252-99
	3,350,317	10/1967	Symes	252-99

30 MAYER WEINBLATT, *Primary Examiner.*

U.S. Cl. X.R.

8-108; 252-95, 186

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,431,206 Dated March 4, 1969

Inventor(s) Thomas B. Hilton & Xavier Kowalski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 40, between the words "are" and "disclosed" insert the word -- not --.  
Column 15, Table II, in column titled "Nitrogen Compound" the line under "Dimethyl Hydantoins" should read -- cyanuric acid --.  
Column 19, claim 3, line 43, after the word "is" and before "pentaisocyanurate" insert --  $\sphericalangle$ (monotrichloro) tetra-(monopotassium dichloro)  $\sphericalangle$  --.  
Column 19, claim 5, line 50, after the word "a" and before "pentaisocyanurate" insert --  $\sphericalangle$ (monotrichloro) tetra-(monopotassium dichloro)  $\sphericalangle$  --.  
Column 20, claim 11, line 62, after the word "is" and before "pentaisocyanurate" insert --  $\sphericalangle$ (monotrichloro) tetra-(monopotassium dichloro)  $\sphericalangle$  --.  
Column 21, claim 14, line 8, after the word "thereof;" and before "di-isocyanurate;" insert --  $\sphericalangle$ (monotrichloro)(monopotassium dichloro)  $\sphericalangle$  --.  
Column 21, claim 14, line 8, after the word "di-isocyanurate;" and before "pentaisocyanurate;" insert  $\sphericalangle$ (monotrichloro) tetra-(monopotassium dichloro)  $\sphericalangle$  --.  
Column 22, claim 15, line 2, after the word "of" and before "pentaisocyanurate;" insert --  $\sphericalangle$ (monotrichloro) tetra-(monopotassium dichloro)  $\sphericalangle$  --.

SIGNED AND  
SEALED  
SEP 15 1970

(SEAL)

Attest:

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Commissioner of Patents