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BLEACHING PACKETS

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ABSTRACT OF THE DISCLOSURE

A bleaching packet in which a dry bleach composition containing a hypochlorite generating agent and inorganic builder salt is enclosed in a film of polyvinyl alcohol impregnated with a water-soluble salt of a strong base and a weak acid. Also, a packet in which a water-soluble, polyvinyl alcohol film encloses a dry bleach composition which contains a mixture of dichloroisocyanurate, carbonate, tripolyphosphate and sulfate salts, said salts being either sodium or potassium and being suitably selected to achieve a weight ratio of potassium to sodium of at least 1:1 in the composition.

This application is a continuation-in-part of my application Ser. No. 563,675 filed July 8, 1966 now abandoned.

The present invention relates to packets of bleaching powder. More particularly, it relates to water soluble packets which contain a water soluble bleaching powder.

In accordanace with the present invention, a bleaching packet comprises a dry water soluble composition which liberates hypochlorite chlorine on contact with water disposed within an envelope of polyvinyl alcohol film impregnated with a water soluble salt of a strong base and a weak acid, i.e., a water soluble alkaline buffer salt, preferably having the ability to act as a reducing agent. The presence of an alkaline buffer salt in the polyvinyl alcohol film of the instant invention is highly beneficial and advantageous in that the instant packets are characterized by improved stability of the bleach content thereof, diminished loss of available chlorine on aging of the packets, diminished formation of insoluble material during storage of the packets, improved maintenance of original color and clarity of the polyvinyl alcohol film during storage and aging the packets, and improved odor characteristics exhibited on use thereof. The instant packets are also characterized by improved maintenance of an original high level of available chlorine and maintenance of original film characteristics on long storage and aging. Minimized film degradation including reduced embrittlement and cracking is a highly desirable characteristic of the packets of the instant invention.

The dry composition within the instant packets comprises a dry water soluble compound which, on contact with water, liberates hypochlorite chlorine, said compound preferably constituting about 1 to 90% by weight of the composition, the remainder, i.e., 10 to 99%, being a water soluble diluent therefor such as water soluble inorganic salt. The inorganic salts used suitably are those alkaline buffer salts which do not react deleteriously with the hypochlorite-generating agent, during either stage or use.

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The instant packets offer the advantage of providing a highly effective chlorine-type bleaching agent in a dry form. These packets avoid the dustiness of powdered products, and the likelihood or dangers of spillage or splattering characteristic of liquid products. In use, the entire packet is dropped into a washing machine containing water and clothes to be bleached without any need for premeasuring by the housewife.

The instant packets also avoid the necessity for handling of bulky containers of glass or fiberboard cartons by the housewife and provide an effective means of making the characteristic and sometimes irritating odor of chlorine-liberating bleaches. Moreover, use of the packets of the instant invention eliminates the possibility of contact of the hypochlorite-liberating bleach with the skin of the user, which is especially desirable in cases of those people who are allergic to hypochlorites.

The instant packets offer the further outstanding advantage that the product container, i.e., the polyvinyl alcohol film in envelope form, contributes considerable soil anti-redeposition properties to the system and thus the instant packets are especially suited for use in conjunction with soap and detergent products in connection with the washing and bleaching of soiled clothes. The use of water soluble polyvinyl alcohol film is also advantageous in that it is thermoplastic and may readily be heat sealed, it offers hi ghresistance to permeability by gases, it has excellent oil and grease resistance, long shelf life, and it can easily be printed with alcohol-type inks.

As indicated above, the polyvinyl alcohol film employed in the preparation of the instant packets is water soluble, that is, with mild agitation it dissolves substantially completely in water at temperatures of from about 80° to 140° F. within about 30 seconds. Commercial polyvinyl alcohol which is prepared by the hydrolysis of polyvinyl acetate may be employed, however, it has been found highly desirable to avoid the use of water soluble polyvinyl alcohol which has been ethoxylated, i.e., reacted with ethylene oxide, inasmuch as such ethoxylated polyvinyl alcohol appears to be less stable on aging and storage in contact with the instant hypochlorite generating agents than does material which is free from ethoxylation. Polyvinyl alcohol which is devoid of ethoxylation and which contains on the order of from about 12–40 percent by weight of unhydrolized vinyl acetate has been found to be desirably stable towards the hypochlorite liberating agent during storage and use and to possess highly valuable flexibility characteristics and solubility characteristics in both hot (140° F.) and cold (80° F.) water.

Hypochlorite generating agents suitable for use in the packets of the present invention are those water soluble dry solid materials which generate hypochlorite ion on contact with, or dissolution in, water. Examples thereof are the dry, particulate heterocyclic N-chloro imides such as trichloroisocyanuric acid, and dichloroisocyanuric acid and salts thereof such as sodium dichloroisocyanurate and potassium dichloroisocyanurate. Other imides may also be used such as N-chlorosuccinimide, N-chloromalonimide, N - chlorophthalimide and N - chloronaphthalimide. Additional suitable imides are the hydantoins such as 1,3 - dichloro 5,5 - dimethyl hydantoin; N-monochloro-5,5 - dimethylhydantoin; methylene-bis (N-chloro-5,5-dimethylhydantoin); 1,3 - dichloro - 5 - methyl - 5 - isobutylhydantoin; 1,3 - dichloro - 5 - methyl - 5 - ethylhydantoin; 1,3 - dichloro - 5,5 diisobutylhydantoin; 1,3 - di-

chloro - 5 - methyl - 5 - n - amylhydantoin, and the like. Other useful hypochlorite-liberating agents are trichloromelamine N,N-dichlorobenzoylene urea, N,N-dichloro-p-toluenesulfonamide and dry, particulate, water-soluble anhydrous inorganic salts such as lithium hypochlorite and calcium hypochlorite. Normally, the instant chlorine-liberating agents are employed in a proportion, within the range, indicated above, such as to yield a product which contains from about 1 to about 20% available chlorine on a total weight basis, although other proportions may be employed if desired. The remainder of the bleaching composition is a water soluble diluent therefor, such as a water soluble inorganic salt, the term "water soluble" being used in the sense of water soluble or dispersible. The diluent itself normally will constitute a material such as an alkaline inorganic buffer salt, e.g., a detergent builder salt, which does not react deleteriously with a hypochlorite-generating agent either during storage or use.

Surface active agents suitable for use in the instant packets include a wide variety of water soluble organic detergents and wetting agents stable in the presence of the hypochlorite generating agent. Such detergents may be anionic detergent salts having alkyl substituents of 8 to 22 carbon atoms such as the water soluble higher fatty acid alkali metal soaps, e.g., sodium myristate and sodium palmitate; water soluble sulfated and sulfonated anionic alkali metal and alkaline earth metal detergent salts containing a hydrophobic higher alkyl moiety (typically containing from about 8 to 22 carbon atoms) such as salts of higher alkyl mono or polynuclear aryl sulfonates having from about 10 to 16 carbon atoms in the alkyl group (e.g., sodium dodecylbenzenesulfonate, magnesium tridecylbenzenesulfonate, lithium or potassium pentapropylenebenzenesulfonate); alkali metal salts of higher alkyl naphthalene sulfonic acids; sulfated higher fatty acid monoglycerides such as the sodium salt of the sulfated monoglyceride of coconut oil fatty acids and the potassium salt of the sulfated monoglyceride of tallow fatty acids; alkali metal salts of sulfated fatty alcohols containing from about 10 to 18 carbon atoms (e.g., sodium lauryl sulfate and sodium stearyl sulfate); alkali metal salts of higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g., fatty acid esters of the sodium salt of isethionic acid; the fatty ethanolamide sulfates; the fatty acid amides of amino alkyl sulfonic acids, e.g., lauric acid amide of taurine; as well as numerous other ionic organic surface active agents such as sodium toluene sulfonate, sodium xylene sulfonate, sodium naphthalene sulfonate, sodium toluene sulfonate; and mixtures thereof. In general these organic surface active agents are employed in the form of their alkali metal salts or alkaline earth metal salts as these salts possess the requisite stability, solubility, and low cost essential to practical utility.

The use of amphoteric, cationic and non-ionic detergents is also contemplated by the present invention. These detergents should, of course, be employed in a compatible proportion and manner, e.g., in encapsulated form, if appropriate.

Examples of amphoteric detergents which may be employed include the fatty imidazolines, such as 2-coco-1-hydroxyethyl - 1 - carboxymethyl - 1 - hydroxyl imidazoline and similar products made by reacting monocarboxylic fatty acids having chain lengths of 10 to 24 carbon atoms with β-hydroxyethyl ethylene diamine and with monohalo monocarboxylic fatty acids having from 2 to 6 carbon atoms, the fatty beta-alanines such as dodecyl beta-alanine, the inner salt of 2-trimethylamino lauric acid, betaines such as N-dodecyl-N,N-dimethylamino acetic acid, and the like. Mixtures of any two or more of the foregoing may be employed.

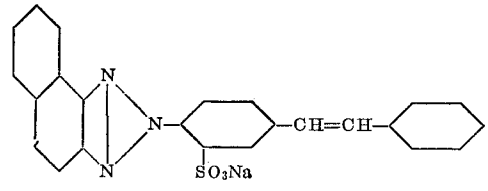
A wide variety of cationic surface active agents may be employed in the compositions of the present invention, including distearyl dimethyl ammonium chloride, stearyl dimethylbenzyl ammonium chloride, coco dimethylbenzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetylpyridinium chloride, cetyltrimethyl ammonium bromide, the stearyl amine salts that are soluble in water such as stearyl amine acetate and stearyl amine hydrochloride, stearyl-dimethylamine hydrochloride, distearyl amine hydrochloride, octyl phenoxyethoxyethyl dimethylbenzyl ammonium chloride, decyl pyridinium bromide, the pyridinium chloride derivative of the acetylaminoethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decylamine acetate, lauryl dimethylbenzyl ammonium chloride, and the like. Mixtures of two or more cationic surface agents may be employed if desired.

Nonionic surface active agents which may be employed include the ethylene oxide ethers of alkyl phenols such as nonyl phenol polyoxyethylene ether, the ethylene oxide ethers of fatty alcohols such as tridecyl alcohol polyoxyethylene ether, the ethylene oxide ethers of alkyl mercaptans such as dodecyl mercaptan polyoxyethylene thioether, the ethylene oxide esters of acids such as the lauric ester of polyethylene glycol and the lauric ester of methoxy polyethylene glycol, the ethylene oxide ethers of fatty acid amides, the condensation products of ethylene oxide with partial fatty acid esters of sorbitol such as the lauric ester of sorbitan polyethylene glycol ether, and other similar materials.

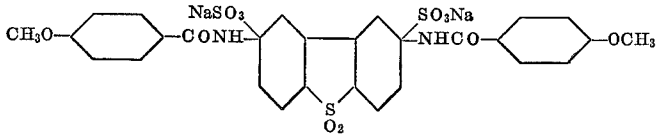
The proportion of organic surface active agent which is used may vary widely, typically being from about 1 to 30% by weight of the composition contained within the packet.

The presence of inorganic salts in the instant bleach packets is desirable in that the inorganic salt may serve to adjust pH and also to act as a carrier or dispersion medium for the bleaching agent and if desired, for any other active agents which are employed. Water soluble salts suitable for use in the instant packets include sodium sulfate, sodium chloride, alkaline detergents builder salts having a pH of from 8 to 11 or above such as sodium carbonate, potassium carbonate, borax, and sodium silicate, alkali metal orthophosphates, and polyphosphates such as monosodium phosphate, trisodium phosphate, tetrasodium pyrophosphate, pentasodium tripolyphosphate, pentapotassium tripolyphosphate and acid salts such as sodium bisulphate. The presence of sodium carbonate, potassium carbonate, or sodium metasilicate in the instant packets has been found to aid in the retention of the water soluble characteristics of these packets, sodium carbonate or potassium carbonate being especially beneficial in that on dissolution in water, it reacts with any acidic components present (e.g., in the hypochlorite generating agent) to produce bubbles of carbon dioxide gas which contribute a desirable mixing and agitating action.

A highly desirable constituent of the composition within the instant packets is a fluorescent brightener or optical dye which is stable in the presence of the hypochlorite generating agent. Such brighteners are of particular assistance in connection with the bleaching of textiles or fabrics in those instances where the chemical bleaching power of the contents of the instant packets may beneficially be supplemented by the action of a blue fluorescing optical bleach. Examples of suitable textile substantive optical bleaches, which may be present in amounts on the order of about 0.1 to 1 percent by weight of the packets, are triazole compounds such as



and sulfonated diaminodibenzenethiophene dioxides such as



The packets of the present invention optionally may also contain suitable proportions, i.e., on the order of 0.1 to 1 percent by weight thereof, of hypochlorite-stable, non-substantive bluing agent such as ultramarine blue. (It will be appreciated, especially in connection with such bluing agent which is a water insoluble pigment, that for the purposes of this invention, materials which are not truly water soluble may be present as long as they are water dispersible in normal use of the instant packets.)

The resistance of the instant packets towards the formation of insoluble material during storage may be improved by sealing these packets within a moisture impermeable container, such as a metal foil or metal foil covered paperboard box and/or within a plastic film characterized by an extremely low moisture vapor transmission rate, e.g., polyethylene; laminates of polyethylene, aluminum foil, and glassine, or wax-coated laminates of metal foil and glassine. A preferred reclosable container which is substantially impermeable to moisture vapor constitutes a bag of polyethylene or like film which is sufficiently large that the open end may be multiply folded over on itself to provide a substantially moisture vapor tight seal. Such a bag having a folded closure may be placed within a more rigid container or otherwise be provided with means to prevent unravelling of the folded portion of the bag.

The compositions within the instant packets should be dry i.e., desirably they contain less than 1% and preferably less than 0.5% moisture, in order to prevent decomposition of the hypochlorite liberating agents prior to use of the packets. Various adjuvants may, however, be present including, inter alia, sodium carboxymethyl cellulose, citric acid, resins and polymers such as polyvinyl pyrrolidone, polyacrylates and the like, starch, urea, perfumes, corrosion inhibitors, coloring matter, and the like.

Preferably, the alkaline buffer salts of the present invention are reducing agents, typically salts of strong bases with weak reducing acids, i.e., water soluble inorganic or organic salts which dissolve in water to form dilute (e.g., 0.25%) solutions having a pH greater than about 8. Examples of such preferred reducing agents are sodium sulfite, sodium nitrite, sodium formate, and sodium hypophosphite. Examples of further suitable reducing agents include sodium metabisulfite, sodium hydrosulfite, sodium thiosulfate, sodium dodecylbenzenesulfinate, sodium toluenesulfinate, potassium sulfite, potassium hydrosulfite, lithium sulfite, rubidium sulfite, magnesium sulfite, and the like. Other suitable alkaline buffer salts include alkali metal salts such as potassium acetate, sodium acetate, and the water soluble inorganic alkali metal detergent builder salts, such as sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium orthosilicate, sodium disilicate, sodium metasilicate, sodium orthophosphate, monohydrogen sodium orthophosphate, dihydrogen sodium orthophosphate, sodium metaphosphate, pentasodium tripolyphosphate, tetrasodium pyrophosphate, disodium dihydrogen pyrophosphate, potassium carbonate, potassium bicarbonate, potassium orthophosphate, monopotassium dihydrogen orthophosphate, dipotassium monohydrogen orthophosphate, dipotassium monohydrogen orthophosphate, tetrapotassium pyrophosphate, potassium metaphosphate, potassium metasilicate, potassium disilicate, potassium hydrogen disilicate, potassium tetrasilicate, lithium carbonate, lithium bicarbonate, lithium orthophosphate, rubidium carbonate, and the like. Alkaline earth metal salts such as magnesium sulfite may also be used.

Suitably the instant buffers may be present in the film in any amount ranging from a small but sufficient amount to inhibit attack on the film by the hypochlorite liberating agent up to an amount which adversely affects the physical properties of the film. Typically, from .5 to 25% and preferably from about 2 to 10% by weight of the buffering agent based on the total weight of the film should be employed. In those cases in which combinations of alkaline buffer salts with the instant reducing agents are employed in the film, suitable proportions typically in the range of from about 1 to 20% thereof may also be employed, the total content of stabilizing element in the film preferably not being greater than about 25% thereof and desirably less than about 15% thereof.

The following examples are given additionally to illustrate the nature of the invention and it will be understood that the invention is not limited thereto. All parts or percentages are by weight unless otherwise indicated, and unless specifically denoted to be otherwise, the components employed are substantially completely dry or anhydrous.

EXAMPLE I

An aqueous solution of commercially available polyvinyl alcohol resin of the type employed for the preparation of water soluble polyvinyl alcohol films is prepared. The resin is of a grade which contains approximately 88 percent hydrolyzed polyvinyl acetate, and the temperature of the solution is about 30° C. Sodium nitrite is dissolved in the solution in a proportion equal to 7% by weight of the resin therein, the total solids content of the final solution being about 25% by weight. The uniform solution is then cast on the surface of a polished stainless steel band to form a film of uniform thickness. The band is heated to about 275° C. to drive off the water in the film. After drying, the cast film is peeled away from the band. The dried film, which is 1.5 mils uniform thickness is then used to prepare packets having measurements of approximately 2.75 x 1.75 inches and weighing about 0.4 gram.

In the preparation of packets, one rectangle of film is placed over a shallow depression in a hollow block. The depression is evacuated, thus drawing the central portion of the film into the depression and forming a pouch or pocket therein. 40 grams of the following compositions are placed in the pouch formed in the film, and the edge portions of the film which protrude from the depression in the block are moistened with water. A second piece of film is then aligned with the first piece and pressed against it to form a closed packet completely enveloping the composition contained therein. Hot air is applied to the surface of the packet to dry the moistened portion thereof, and the completed bleaching packet, after breaking the vacuum, is removed from the block on which it is formed.

The composition encased within the package is as follows:

	Parts by weight
Potassium dichloroisocyanurate	21.5
Pentasodium tripolyphosphate	30
Sodium carbonate	5
Sodium sulfate	40.5
Sodium dodecylbenzenesulfonate	2
Sodium silicate	.5
Perfume and coloring, balance to 100.	

The packets so produced show excellent stability with respect to retention of original chlorine content, water

solubility, color, odor, flexibility, and other properties on long storage and on accelerated aging at elevated temperatures, e.g., 130° F.

EXAMPLES II–IV

Packets corresponding to those described in Example I are prepared with the modifications (a) that sodium sulfite is added to the solution of the resin in an amount equal to 10% by weight of the resin solids in lieu of the sodium nitrite of Example I and (b) the following respective compositions are employed within the packets.

	Parts by weight		
	II	III	IV
Potassium dichloroisocyanurate	20	17	17
Potassium tripolyphosphate	30		
Sodium tripolyphosphate		30	30
Potassium carbonate	5		
Sodium carbonate		5	
Potassium sulphate	45		
Sodium sulphate		47.7	53
Ultramarine blue		0.3	

EXAMPLE V

Packets containing the same coposition as given in Example I are prepared with the modification that sodium acetate in amounts equal to 5% or 10% by weight of resin solids is used in the film instead of sodium nitrite. Other than for slightly less desirable color and possibly less flexibility, the desirable properties obtained in Example I are achieved.

EXAMPLE VI

Packets are prepared in accordance with the process of Example I employing 5% sodium nitrite as the reducing agent added to the film. The following composition is enveloped within packets thereof:

	Parts by weight
Trichloroisocyanuric acid	14
Dipotassium isocyanurate	12.2
Potassium carbonate	8.3
Potassium tripolyphosphate	30.0
Potassium sulphate	35.5

These packets show substantially improved retention of original properties over comparable packets prepared and enveloping the same chlorine-yielding composition but with the stabilizer omitted from the film. Even better results are obtained if the sodium nitrite content is increased to 10% by weight of the polyvinyl alcohol.

EXAMPLE VII

Similar results as the foregoing are achieved when the composition within the packets of Example I is as follows:

	Parts by weight
Trichloroisocyanuric acid	14
Trisodium isocyanurate	11.5
Potassium carbonate	8.3
Potassium tripolyphosphate	30.0
Potassium sulphate	36.2

EXAMPLE VIII

Commercial polyvinyl alcohol film-forming resin is dissolved in water and 10% sodium sulfite is added thereto, the percentage being calculated on the basis of the polyvinyl alcohol resin solids content of the solution. The solution is cast into film about 1.5 mils thick, and packets are formed therefrom in accordance with Example I. The packets are filled with about 40 grams each of the following composition:

	Parts by weight
Trichloroisocyanuric acid	14
Potassium monohydrogen phosphate	40
Potassium carbonate	5
Sodium sulfate	41

EXAMPLES IX AND X

The sodium sulfite of Example VIII is replaced by 7% sodium sulfite and 4% sodium carbonate. Into the packets so prepared was introduced respectively 32 g. of trichloroisocyanuric acid and 8 g. of potassium dichloroisocyanurate (Example IX) and mixture of 20 g. of trichloroisocyanuric acid and 20 g. of potassium dichloroisocyanurate (Example X). The packets are aged at 140° F. for several days, and are compared for film solubility to similarly filled packets formed only from the resin per se. In both cases the film modified with sulfite and carbonate shows much greater solubility than film without the additive system.

EXAMPLE XI

Packets corresponding to those of Example II are prepared with the modifications (a) that 7% sodium nitrite and 3% disodium monohydrogen phosphate are added to the film in lieu of the inhibitor of that example and (b) that the following bleach compositions are used in these packets.

	Parts by weight	
	A	B
Potassium dichloroisocyanurate	21.3	20
Sodium tripolyphosphate	30.0	10
Sodium sulphate	40.3	70
Sodium carbonate	5	
Sodium dodecylbenzenesulfonate	2.6	
Mineral oil	0.4	
Ultramarine blue	0.3	
Perfume	0.1	

The packets so prepared show excellent stability and retention of original properties.

EXAMPLE XII

Packets are prepared using various inhibited films to envelope the following composition:

	Parts by weight
Potassium dichloroisocyanurate	16
Pentasodium tripolyphosphate	40
Sodium tridecylbenzenesulfonate	2
Ultramarine blue	0.3
Sodium sulfate, balance to 100.	

The films employed constitute commercial polyvinyl alcohol film devoid of ethoxylation and containing about 12% of unhydrolyzed acetate. Packets are prepared using films modified with the inhibitors and combinations of inhibitors in the proportion by weight indicated:

	Percent
(A)	
$NaNO_2$	5
$NaNO_2$	7
(B)	
$NaNO_2$	7
$Na_3PO_4 \cdot 12H_2O$	3
(C)	
$NaNO_2$	7
$Na_2HPO_4 \cdot 7H_2O$	1.5
(D)	
$NaNO_2$	7
$Na_2SiO_3 \cdot 9H_2O$	7
(E)	
$NaNO_2$	5
$Na_3PO_4 \cdot 12H_2O$	1.5
(F)	
$NaNO_2$	5
$Na_2HPO_4 \cdot 7H_2O$	1.5
(G)	
$NaNO_2$	7
K_3PO_4	3

(H)

	Percent
KNO_2	7
K_2HPO_4	3

(I)

KNO_2	7
$Na_5P_3O_{10}$	3

These packets exhibit excellent storage and aging characteristics.

EXAMPLE XIII

Four sets of packets are prepared in accordance with Example I hereof with the modification that sodium sulfite is added to the polyvinyl alcohol resin solution in amounts equal to (A) 1, (B) 5, (C) 10, and (D) 20% by weight of the resin respectively. Packets are prepared from each of these various films in accordance with Example I with the further modification that the compositions packaged therein contain the following:

	Parts by weight
Potassium dichloroisocyanurate	20
Sodium sulfate	70
Pentasodium tripolyphosphate	10

The finished packets of each set are stored in polyethylene bags which are hermetically sealed. On aging the packets exhibit excellent stability with respect to available chlorine content, formation of insoluble products, discoloration, flexibility and formation of malodors, the packets prepared from films having the highest content of inhibitor exhibiting the best characteristics.

Three additional sets of packets are prepared from polyvinyl alcohol films which contain 5, 10, and 20% by weight of sodium dodecylbenzene sulfinate in lieu of the same proportion of sodium sulfite referred hereinabove in this Example. These packets exhibit excellent storage stability.

Comparable results are obtained using the above films containing either sodium sulfite or sodium dodecylbenzene sulfinate but modified in that the composition within the packet consists of 10 grams of potassium dichloroisocyanurate.

EXAMPLE XIV

Packets measuring approximately 2.75 x 1.75 inches are prepared from film containing about 93.5 parts of commercial polyvinyl alcohol in which the resin is prepared by hydrolysis of polyvinyl acetate, the hydrolysis being approximately 88% complete and the film having a content of unhydrolyzed polyvinyl acetate of approximately 12% by weight, and 6.5 parts by weight of sodium hypophosphite monohydrate.

The 40 g. composition enveloped within these packets is as follows:

	Parts by weight
Trichlorisocyanuric acid	16
Pentasodium tripolyphosphate	20
Potassium carbonate	7
Sodium tridecylbenzenesulfonate	2
Ultramarine blue	0.33

Sodium sulphate anhydrous, balance to 100.

Packets thus prepared show a high degree of solubility upon storage relative to packets containing the same bleach composition but without additive, in the film.

EXAMPLES XV–XVII

Packets prepared according to Example I using modified film to contain about 7% by weight of disodium hydrogen phosphite, sodium thiocyanate and sodium arsenite respectively are used to enclose 40 g. of the following composition:

	Percent
Trichloroisocyanuric acid	14
Sodium tripolyphosphate	20
Potassium carbonate	7
Ultramarine blue	0.3

Balance to 100% sodium sulfate.

Packets prepared from the modified films described in this example are found to be less subject to the formation of insoluble film than packets prepared with identical film from which the additives mentioned above are omitted.

EXAMPLES XVIII–XX

Packets are prepared according to Example I using film containing respectively:

(a) 10% sodium sulfite (Example XVIII)
(b) 10% sodium nitrite (Example XIX)
(c) 7% sodium nitrite plus 1.5% disodium hydrogen phosphate (Example XX)

as the additives 40 g. of the following composition were sealed therein:

	Parts by weight
Potassium dichloroisocyanurate	16.4
Pentasodium tripolyphosphate	40.0
Sodium lauryl sulfate	1.6
Sodium sulfate	41.5
Ultramarine blue	0.3

Packets so prepared exhibit excellent stability on storage and aging.

EXAMPLES XXI–XXVI

The following composition is prepared:

	Parts by weight
Trichloroisocyanuric acid	14
Dipotassium hydrogen phosphate	40
Potassium carbonate	5
Potassium sulfate	41

Forty gram samples of the foregoing composition are sealed in packets prepared (in accordance with Example I) from commercially available polyvinyl alcohol resin to which is added the following, separate runs of film being prepared with each additive or combination of additives indicated.

Example:

XXI ——— 10% of sodium sulfite.
XXII ——— 10% trisodium phosphate.
XXIII ——— 7% potassium nitrite+3% trisodium phosphate.
XXIV ——— 7% sodium nitrite+3% sodium silicate.
XXV ——— 3% sodium sulfite+3% sodium nitrite +3% disodium hydrogen phosphate.
XXVI ——— 3% sodium sulfite+3% sodium nitrite +3% trisodium phosphate.

The composition used in Examples XXI–XXVI is modified to provide the following compositions:

	Parts by weight		
	A	B	C
Trichloroisocyanuric acid	14	14	14
Potassium tripolyphosphate	20	20	40
Potassium carbonate	7	7	5
Sodium sulfate	59	59	———
Potassium sulfate			41

Bleach packets containing the above compositions and the additive systems listed Examples XXI–XXVI exhibit minimal tendency towards formation of water insoluble material.

EXAMPLE XXVII

Commercial polyvinyl alcohol resin containing 12% unhydrolyzed polyvinyl acetate is modified by the addition thereto of 5% sodium sulfite. The resin is cast into film form and dried to form water soluble film approximately 1.5 mils in thickness. Sheets of this film 2.75 x 1.75 inches

are heat sealed at their edges to thereby enclose about 40 grams of the following bleach composition.

	Parts by weight
Lithium hypochlorite	34
Sodium sulfate	66

The bleaching so formed exhibits improved stability on storage and aging.

EXAMPLES XVIII–XXIX

The following bleach compositions are prepared:

	Parts by weight	
	XXVIII	XXIX
Trichloroisocyanuric acid	14	14
Potassium tripolyphosphate		20
Sodium tripolyphosphate	30	
Potassium carbonate	7	7
Sodium sulfate	49	59

Into film packets modified with 7% sodium nitrite plus 7% sodium metasilicate nonahydrate are placed 40 g. of each composition (Examples XXVII and XXVIII respectively). The packets are aged concurrently with the same bleach systems contained in regular film (without additive). Film solubility of the aged packets under home laundry conditions is satisfactory only when the compositions were enclosed in the additive film.

EXAMPLES XXX–XXXII

The composition of Example XXIX is modified to contain 20% sodium tripolyphosphate instead of 30% sodium tripolyphosphate. With packets prepared from film containing—

Example:

XXXX ---- 7% sodium nitrite plus 7% sodium silicate nonahydrate.

XXXI ---- 7% sodium nitrite plus 3% sodium phosphate dodecahydrate.

or

XXXII ---- 7% sodium nitrite plus 3% sodium carbonate.

the desirable properties described in Example 1 are achieved.

The use of a buffer salt of a strong base and a weak acid in combination with a reducing agent is particularly desirable when the bleaching agent is trichlorisocyanuric acid.

EXAMPLE XXXIII

In any of the modified polyvinyl alcohol film packets described above, the following bleach composition is inserted: 20% sodium dichloroisocyanurate, 40% sodium tripolyphosphate and 40% sodium sulfate.

In accordance with another aspect of this invention there are provided packets having exceptional stability with respect to available chlorine content even under conditions of high humidity, by formulating the mixtures enclosed within the polyvinyl alcohol film so that said mixtures contain dichloroisocyanurates and builder salts in such amounts as to include certain proportions of potassium salts and predetermined sodium: potassium ratios. Mixtures characterized by these proportions and ratios may be enclosed in either the preferred polyvinyl alcohol film containing the alkaline buffer salt, as described above, or less desirably, in polyvinyl alcohol film which does not contain the buffer salt. In the latter case, however, it is found that the use of these mixtures of controlled potassium content gives film packets whose film material has less tendency to become insoluble on storage than when mixtures of lower potassium content and higher sodium: potassium ratio are employed in the same unbuffered film. This improvement in both the chlorine stability and the maintenance of film solubility was surprising and not predictable from the teachings of the prior art.

More particularly, in working with compositions for use in film packets, which compositions contain the sodium or potassium salt of dichloroisocyanuric acid (usually in amount such as to supply about 10–15% of available chlorine) and contain builder salts including tripolyphosphates and carbonates, it has been found that the compositions have very good stability with respect to available chlorine content when the weight ratio of potassium to sodium is at least 1:1. It has also been found that while there is a very marked improvement when the weight ratio of potassium to sodium is raised from say 0.1 to 0.25 or even 0.8:1 to the preferred level of at least about 1:1 (e.g. 1.1:1), there is little if any further improvement when this ratio is raised to much above 1:1, e.g., to about 8:1 or to about 17:1 or to infinity (i.e., when no sodium is present). This is an important finding inasmuch as potassium salts are much more expensive than the corresponding sodium salts. Thus by using a ratio of potassium to sodium closer to 1:1 (e.g., within the range of 1:1 to 10:1, preferably 1:1 to 5:1 or 1:1 to 2:1) one can attain the desired high degre of stability without undergoing the greatly increased expense which would result from the use of much higher ratios of potassium to sodium.

In the most preferred compositions, the proportion of available chlorine is in the range of about 11 to 14% (eg., 12 or 13%), the proportion of the dichloroisocyanurate salt being about 20% of the total composition, and there are present relatively large amounts of a tripolyphosphate (the sodium and/or potassium tripolyphosphates constituting for example more than 25% (e.g,. about 25–35%) of the total composition), a smaller amount (e.g., about 1 to 10% of the total composition) of sodium or potassium carbonate, and relatively large amounts of a sulfate, or other neutral salt (the sodium and/or potassium sulfates constituting for example about 40–70% of the total composition). The total amount of sodium and potassium (calculated in terms of the amount of the element, which is, however, present in the form of its salt, of course) is preferably above 20% and more preferably above 25%, e.g., about 30–40%, of the total composition, and the total amount of potassium is preferably correspondingly above 10%, more preferably above 15% (e.g., about 17%) of the total composition. The amount of "available chlorine," in a composition where all the chlorine is present as the dichloroisocyanurate, is equal to twice the actual chlorine percentage; this is the conventional way of expressing the "available chlorine" which is an indication of bleaching power.

In film packets made with the unbuffered polyvinyl alcohol film the presence of the carbonate in the composition is particularly important since it decreases the tendency for the film to become insolubilized. Also, the carbonate has a beneficial effect in promoting the disintegration of the composition on contact with the wash water.

An all-potassium formulation is illustrated in Example II above. Another formulation in which the potassium: sodium ratio is only about 1.1:1 and which shows a chlorine retention (as measured by exposing the formulation to an atmosphere of 90% relative humidity at a temperature of 90° F. for 4 days) almost as good as that shown by the all-potassium formulation, contains 45 parts of sodium sulfate in place of the potassium sulfate of Example II. Still another formulation which shows a chlorine retention (measured as indicated above) at least as good as the composition of Example II, is identical with Example II except that 20 parts of sodium dichloroisocyanurate are used in place of the 20 parts of potassium dichloroisocyanurate and 5 parts of sodium carbonate are used in place of the 5 parts of potassium carbonate. Each of these formulations may be enclosed in the buffer-containing polyvinyl alcohol film described in the above examples or, as previously indicated, it may be enclosed, less desirably, in an otherwise identical film from which the buffer has been omitted. While in each of the fore-

going specific embodiments any given anion is attached to a single cation, it will be understood that this is by no means an essential condition and that compositions may be used in which there are mixtures of two salts of the anion, e.g., a mixture containing both potassium sulfate and sodium sulfates, or both potassium carbonate and sodium carbonate, both potassium dichloroisocyanurate and sodium dichloroisocyanurate or any combination of these. Of course, the other auxiliary ingredients previously mentioned in this application may be present, such as the detergent shown in Example XII and the coloring materials, brighteners, etc.

Another aspect of this invention, relates to the use of trichlorocyanuric acid in combination with potassium carbonate, in proportion of about 1/10 to 1/2, preferably about 1/5 to 1/2, part of potassium carbonate per part of trichlorocyanuric acid; compositions corresponding to this aspect of the invention are disclosed in Examples VI, VII, VIII, XIV, to XVII, XXI to XXVI, XXVIII to XXXII. The preferred compositions also contain pentasodium tripolyphosphate and sodium sulfate, each in proportion of at least 35%. The potassium carbonate inhibits the formation of obnoxious odors on storage of dry bleach compositions containing trichlorocyanuric acid, and, when the weight ratio of potassium carbonate to trichlorocyanuric acid is within the range described above, the compositions have good stability with respect to chlorine retention. When the weight ratio of potassium carbonate to trichlorocyanuric acid is above about 0.5:1, the stability with respect to chlorine retention is adversely affected.

In the various aspects of this invention it is preferred that the available chlorine contents of the compositions used in the packets preferably be within the range of about 5–20%, more preferably in the range of about 7–15%, and still more preferably above 10%. As previously indicated the percentage of "available chlorine" is, according to the conventional practice in the art of bleaching compositions, twice the actual percentage of active chlorine; thus a typical commercial grade of trichlorocyanuric acid has an "available chlorine" content of 90.2%.

In Example XXXIII the dry bleach composition, which contains sodium dichloroisocyanaurate and is free of carbonate, has good chlorine solubility and disperses readily in the wash water. The presence of the buffer in the polyvinyl alcohol film protects the film against the insolubilizing effects of the composition of that example.

As used herein, the term "hypochlorite chlorine" refers to chlorine present as hypochlorous ion (OCl^-), as is conventional in the art.

What is claimed is:

1. A bleaching packet which consists essentially of a dry, water-soluble, bleaching composiiton; 1–90% by weight of said bleaching composition being a bleaching agent which generates hypochlorite ion on contact with water selected from the group consisting of heterocyclic N-chloro imides, trichloromelamine, N,N-dichlorobenzoylene urea, N,N - dichloro - p - toluene sulfonamide, lithium hypochlorite and calcium hypochlorite, 10 to 99% by weight thereof being water-soluble, alkali metal, inorganic builder salt, and less than 1% by weight thereof being moisture; said bleaching composition being disposed within an envelope of water-soluble, non-ethoxylated, polyvinyl alcohol film containing about 12 to 40% by weight of unhydrolyzed vinyl acetate, said film being impregnated with a water-soluble salt of a strong base and a weak acid selected from the group consisting of organic and inorganic salts having a pH greater than about 8 at a 0.25% salt concentration in water, the amount of impregnating salt being selected from the range of 0.5 to 25% by weight, based on the total weight of the film, and being effective to inhibit insolubilization of said film.

2. bleaching packet as set forth in claim **1** in which the water soluble salt of the strong base and the weak acid is a reducing agent.

3. A bleaching packet as set forth in claim **1** in which said water-soluble salt of a strong base and a weak acid is a mixture of a reducing agent and an inorganic, alkali metal, buffer salt selected from the group consisting of acetates, carbonates, phosphates and silicates.

4. A bleaching packet as in claim **1** in which the composition contains trichlorocyanuric acid in an amount sufficient to provide 5 to 20% by weight of available chlorine and about 1/5 to 1/2 part of potassium carbonate per part of trichlorocyanuric acid.

5. A packet as in claim **1** in which the polyvinyl alcohol is partially hydrolyzed polyvinyl acetate, the hydrolysis being about 88% complete.

6. A bleaching packet consisting essentially of a dry, water-soluble composition; 1–90% by weight of said bleaching composition being a hypochlorite liberating agent selected from the group consisting of trichlorocyanuric acid, dichlorocyanuric acid, potassium dichloroisocyanurate, sodium dichloroisocyanurate and mixtures thereof, 10 to 99% by weight thereof being water-soluble, alkali metal, inorganic builder salt, and less than 1% by weight thereof being moisture, said bleaching packet being disposed within an envelope of water-soluble, non-ethoxylated, polyvinyl alcohol film containing about 12 ot 40% by weight of unhydrolyzed vinyl acetate, said film being impregnated with sodium hypophosphite, the amount of hypophosphite being selected from the range of 0.5 to 25% by weight, based on the total weight of the film, and being effective to inhibit insolubilization of the film.

7. A bleaching packet which consists essentially of a dry, water-soluble bleaching composition; 1–90% by weight of said bleaching composition being a dry, solid heterocyclic N-chloro-imide bleach which generates hypochlorite ion on contact with water, 10 to 99% by weight thereof being water-soluble, alkali metal, inorganic builder salt, and less than 1% by weight thereof being moisture, said bleaching packet being disposed within an envelope of water-soluble non-ethoxylated, polyvinyl alcohol film containing about 12 to 40% by weight of unhydrolyzed vinyl acetate, said film being impregnated with a water-soluble salt of a strong base and a weak acid selected from the group consisting of organic and inorganic salts having a pH greater than about 8 at a 0.25% salt concentration in water, the amount of impregnating salt being selected from the range of 0.5 to 25% by weight, based on the total weight of the film, and being effective to inhibit insolubilization of the film.

8. A bleaching packet as set forth in claim **7** in which said salt is disodium hydrogen phosphite.

9. A bleaching packet as set forth in claim **7** is sodium nitrite.

10. A bleaching packet as set forth in claim **7** in which said salt is sodium sulfite.

11. A bleaching packet as set forth in claim **7** in which said imide is trichloroisocyanuric acid.

12. A bleaching packet as set forth in claim **7** in which said imide is potassium dichloroisocyanurate.

13. A packet as in claim **7** in which said imide is sodium dichloroisocyanurate.

14. A bleaching packet as set forth in claim **7** in which said film also contains sodium carbonate.

15. A bleaching packet which consists essentially of (A) a dry, water-soluble, bleaching composition consisting essentially of (1) a hypochlorite generating agent selected from the group consisting of potassium dichloroisocyanurate, sodium dichloroisocyanurate, and mixtures thereof in an amount sufficient to provide 5 to 20% by weight of available chlorine; (2) 1 to 10% by weight of sodium or potassium carbonate; (3) less than 1% by weight of moisture; and (4) the balance being substantially a mixture of water-soluble, inorganic, sodium or potassium tripolyphosphate and soidum or potassium sulfate; the total amount of potassium calculated in terms of the element being above 10% by weight of the composition and the weight ratio of potassium to sodium being at least 1:1; disposed within (B) an envelope of water-

soluble, non-ethoxylated, polyvinyl alcohol film containing about 12 to 40% by weight of unhydrolyzed vinyl acetate.

16. A bleaching packet as in claim **15** in which the amount of available chlorine in the dichloroisocyanurate is about 11 to 14% of the composition and the sodium or potassium tripolyphosphate comprises at least ¼ of said composition.

17. A packet as in claim **15** in which the polyvinyl alcohol is partially hydrolyzed polyvinyl acetate, the hydrolysis being about 88% complete.

18. A bleaching packet as in claim **16** in which said composition contains at least about 40% of sodium or potassium sulfate.

19. A bleaching packet as in claim **16** in which said potassium:sodium ratio is 1:1 to 10:1.

20. A bleaching packet as in claim **18** in which said potassium:sodium ratio is 1:1 to 10:1 and the total concentration of sodium and potassium in said composition is about 30–40%, said neutral salt comprising sodium or potassium sulfate.

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MAYER WEINBLATT, Primary Examiner

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