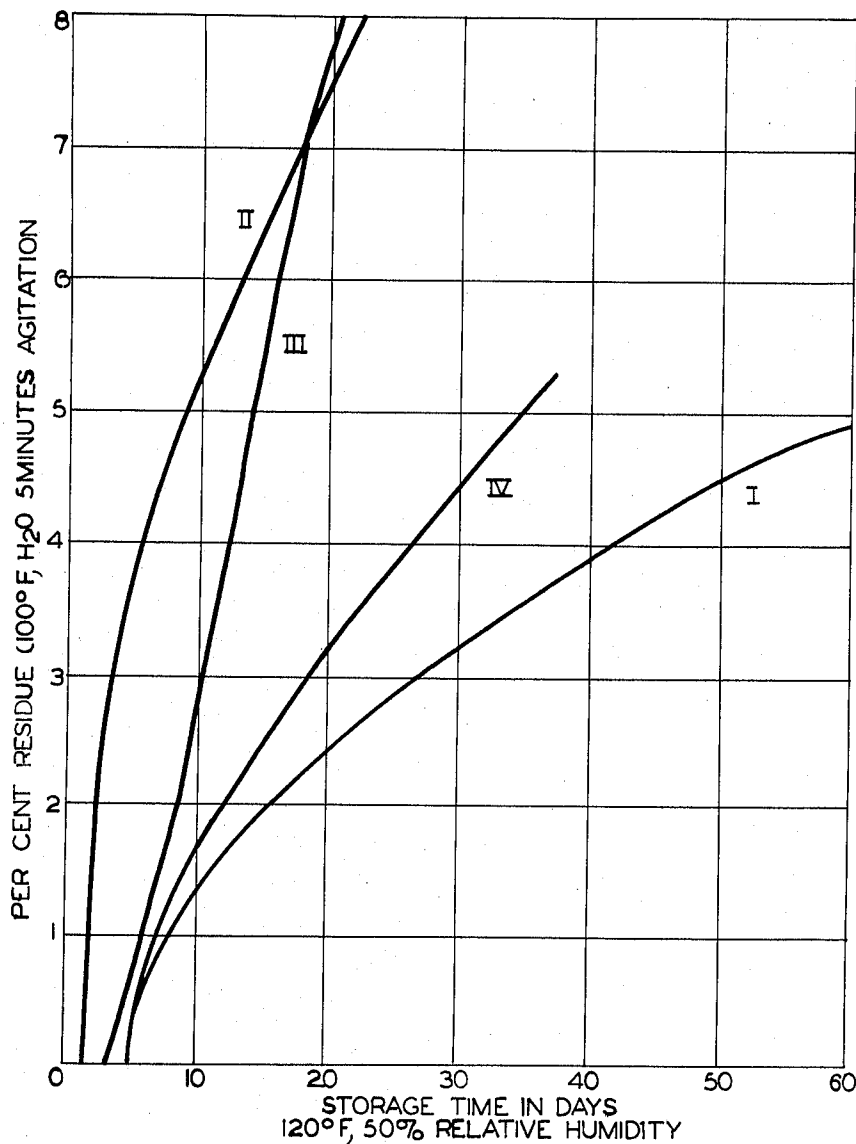


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ESTERS OF ETHOXYLATED ALKYL PHENOLS AND
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POLYVINYL ALCOHOL COMPOSITION WITH PHOSPHATE ESTERS OF ETHOXYLATED ALKYL PHENOLS AND POLYOXYETHYLENE ARYL ETHER

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This invention relates to a polyvinyl alcohol composition having improved resistance to chlorine-containing bleaches. More particularly, the invention concerns soluble polyvinyl alcohol film suitable for the packaging of chlorine-containing bleaches.

Water soluble polyvinyl alcohol films have come into extensive use for the packaging of commercial and household detergents, soaps, disinfectant preparations, laundry starch and bluing, and like products. Such films are conventionally prepared by casting or extruding into film thicknesses, mixtures of polyvinyl alcohol and suitable plasticizers and fillers. While the known soluble polyvinyl alcohol films have proved suitable for packaging the type of products mentioned, they have evinced undesirable characteristics when attempts have been made to employ them for prepackaging of chlorine-containing dry bleaches. These undesirable characteristics have included instability and deterioration of the film in contact with the bleaching agent, and a loss of cold water solubility and of flexibility at low temperatures. Accordingly, there has existed a need for a water soluble polyvinyl alcohol which would be suitable for packaging of chlorine-containing bleaches and which would possess stability toward the bleach, outstanding cold water solubility, stability toward aging, and durability at low temperatures.

In accordance with the present invention, there is provided a polyvinyl alcohol composition having improved resistance to chlorine-containing bleaches, and which in film form is especially suited for the packaging of such bleaches. The polyvinyl alcohol which is employed for packaging chlorine-containing bleaches, in accordance with the invention, is one which is characterized as cold water sensitive, by which is meant that the polyvinyl alcohol tends to soften or swell in cold water, although not necessarily to dissolve completely. By cold water is meant water at a temperature up to about 90° F. Thus, for practical purposes a suitable packaging film would be one which, when made into a plastic bag, and filled with a given material, will release its contents in about 1 minute or less when immersed in water at a temperature of about 90°–100° F.

The polyvinyl alcohol composition of the invention, which combines the foregoing cold water sensitivity or solubility characteristics with resistance toward chlorine-containing dry bleaches comprises an incompletely hydrolyzed polyvinyl alcohol, together with from about 5 to about 30 percent by weight, based upon the weight of the polyvinyl alcohol, of a polyoxyethylene aryl ether. There may also be included in the composition from about 5 to about 50 percent by weight, based upon the weight of the polyvinyl alcohol, of a plasticizing agent, for example, an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol. The preferred polyvinyl alcohol is a 75 to 90% hydrolyzed polyvinyl acetate product of medium molecular weight and medium viscosity. A polyvinyl alcohol of this type, about 80–83% hydrolyzed, is sold commercially under the designation Vinol 624 by Air Reduction Chemical and Carbide Company.

The polyoxyethylene aryl ether appears itself to perform a plasticizing function. It is preferably an ethoxylation product of phenol or substituted phenol. Ethoxylated

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phenol of the type sold commercially under the designation Pycal 94 by Atlas Chemical Industries, is the preferred type of purposes of the invention.

The alkali metal salts of mixed phosphate esters of an ethoxylated higher phenol form a class of plasticizers which is prepared by the neutralization of an approximately equimolecular mixture of the mono- and di-phosphate esters of ethoxylated higher alkyl phenols. The preferred compound of this class for the purposes of the invention is the sodium salt of a mixture of ethoxylated nonylphenol phosphates, which is sold commercially under the designation Gafac LO 529 by Antara Chemicals Division of General Aniline and Film Corporation.

A cold water sensitive polyvinyl alcohol film composition of the invention is prepared by dissolving the resin in water, adding one or both plasticizers to the solution and agitating until the mixture forms a homogeneous liquid, and casting or extruding the liquid into a film, in accordance with conventional procedures in this art. Film thickness can range from 0.5 to 10 mils.

The polyvinyl alcohol compositions of the invention have the following typical properties:

Film thickness (mils) -----	1.5
Yield (sq. yds. per lb.) -----	10.5–13.0
Tensile strength (p.s.i.) -----	4,500–8,500
Moisture content (percent) -----	2.5–4.5
100% modulus (force required to double the length) -----	1,500–4,000
Elongation (percent) -----	300–600
Heat seal temperature, ° F. -----	330–400
Solution behavior (90° F. water)	
Agitated:	
Time for complete solution (sec.) -----	100–150
Time for package rupture (sec.) -----	20–40
Static:	
Time for package rupture (sec.) -----	20–40

The polyvinyl alcohol film compositions of the invention exhibit outstanding stability toward conventionally used dry bleaching agents such as potassium dichloroisocyanurate.

The invention thus enables packets containing household bleaches to be prepared, which will provide pre-measured amounts of the bleach, which will not lose their water solubility characteristics upon storage, and which will protect the contents of the packet from exposure to the atmosphere.

The outstanding unexpected stability toward chlorine-containing bleaches of packets made with polyvinyl alcohol film of the invention is clearly demonstrated in the curves of the accompanying drawing. The curves indicate the rate of development of insoluble residue in packets containing a household type chlorine dry bleach, 15% potassium dichloroisocyanurate, which were aged under accelerated conditions at 120° F. and 50% relative humidity. Under these conditions, packets made with the film of the invention (curves I and IV) required 35 to 60 days to develop about 5 percent residue, while two other commercial films (II and III) tested showed the same degree of insolubilization in only 8 to 15 days.

The preparation of the polyvinyl alcohol films of the invention is illustrated by the following examples:

Example 1

500 lb. of a medium molecular weight, incompletely hydrolyzed polyvinyl alcohol are added to 150 gallons of soft water in a high-speed mixing tank and mixed for 45 minutes at 280 r.p.m. Then there are added 75 lb. of ethoxylated phenol (Pycal 94) and 105 lb. of the sodium salt of a mixture of ethoxylated nonylphenol phosphates, and the mixture is agitated for another 15 minutes. The mixing temperatures are 190° to 205° F. The batch is then pumped to a holding tank for blending and deaera-

tion. A dye, such as anthraquinone blue, may be added to the solution in the holding tank. The blending time is 30 minutes, and the deaeration time is 22.5 hours. In the holding tank moderate agitation at 12-16 r.p.m. is maintained.

The film composition is cast from the deaerated solution onto a stainless steel belt and the resulting film is dried by passing through an oven. The dry film is then cooled, stripped from the belt, and cut to the desired size.

Example 2

A preferred embodiment of the invention is prepared as described in Example 1, employing 100 parts by weight of medium molecular weight approximately 80-83% hydrolyzed polyvinyl alcohol (Vinol 624), 15 parts by weight of ethoxylated phenol (Pycal 94), and 21 parts by weight of the sodium salt of a mixture of ethoxylated nonylphenol phosphates (Gafac LO-529).

The product showed a high resistance to a chlorine-containing bleach, potassium dichloroisocyanurate, on aging for 30 days at 120° F. and 50% relative humidity, developing a residue of only 3.5% (see curve I of the drawing).

Example 3

100 parts by weight of a medium molecular weight approximately 80-83% hydrolyzed polyvinyl alcohol (Vinol 624) and 25 parts by weight of ethoxylated phenol (Pycal 94) were added to 30 gallons of water and processed as described in Example 1. The product, when converted to film, showed a high resistance to a chlorine-containing bleach on aging for 30 days at 120° F. and 50% relative humidity, developing a residue of only 4.5% (see curve IV of the drawing).

While present preferred embodiments of the invention have been described herein, the invention may be otherwise variously embodied and practiced within the scope of the following claims.

What is claimed is:

1. A polyvinyl alcohol film forming composition which is resistant to chlorine-containing bleaches, comprising an incompletely hydrolyzed polyvinyl alcohol, and, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of a polyoxyethylene aryl ether, and from about 5% to about 50% of an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol.

2. A cold water sensitive polyvinyl alcohol film forming composition which is resistant to chlorine-containing bleaches, comprising an incompletely hydrolyzed polyvinyl alcohol, and, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of ethoxylated phenol, and from about 5% to about 50% of the sodium salt of a mixture of ethoxylated nonylphenol phosphates.

3. A polyvinyl alcohol film soluble in water having a temperature up to about 90° F. and which is resistant to chlorine-containing bleaches, comprising an incompletely hydrolyzed polyvinyl alcohol, and, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of a polyoxyethylene aryl ether, and from about 5% to about 50% of an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol.

4. A polyvinyl alcohol film soluble in water having a temperature up to about 90° F. and which is resistant to

chlorine-containing bleaches, comprising a medium molecular weight 75% to 90% hydrolyzed polyvinyl alcohol, and, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of ethoxylated phenol, and from about 5% to about 50% of the sodium salt of a mixture of ethoxylated nonylphenol phosphates.

5. A polyvinyl alcohol film soluble in water having a temperature up to about 90° F. and which is resistant to chlorine-containing bleaches, comprising 100 parts by weight of a medium molecular weight approximately 80% to 83% hydrolyzed polyvinyl alcohol, about 15 parts by weight of ethoxylated phenol, and about 21 parts by weight of the sodium salt of a mixture of ethoxylated nonylphenol phosphates.

6. A polyvinyl alcohol film forming composition which is resistant to chlorine-containing bleaches, comprising an incompletely hydrolyzed polyvinyl alcohol, and, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of a polyoxyethylene aryl ether and an amount of an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol sufficient to plasticize said composition.

7. Process for the preparation of a cold water sensitive polyvinyl alcohol film forming composition which is resistant to chlorine-containing bleaches, which comprises the steps of dissolving an incompletely hydrolyzed polyvinyl alcohol in water, adding to the resulting solution, based upon the weight of the polyvinyl alcohol, from about 5% to about 30% by weight of a polyoxyethylene aryl ether, and an amount of an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol sufficient to plasticize said composition, and agitating the mixture at a temperature between about 190° and 205° F., and deaerating the mixture.

8. Process for the preparation of a cold water sensitive polyvinyl alcohol film forming composition which is resistant to chlorine-containing bleaches, which comprises the steps of dissolving an incompletely hydrolyzed polyvinyl alcohol in water, adding to the resulting solution based upon the weight of the polyvinyl alcohol, from about 5% to about 30% of a polyoxyethylene aryl ether, and from about 5% to about 50% of an alkali metal salt of mixed phosphate esters of an ethoxylated higher alkyl phenol, agitating the mixture at a temperature between about 190° and 205° F., and deaerating the mixture.

9. The process of claim 8 in which the polyvinyl alcohol composition is cast in film form and dried.

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