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PROCESS OF BLEACHING TEXTILES WITH LOWER ALKYL QUATERNARY AMMONIUM PERHALIDES

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4 Claims. (Cl. 8—108)

This invention relates to organic bleaching compositions having advantageous properties.

Compounds and compositions capable of releasing chlorine have long been known and used for bleaching and stain removal. Inorganic hypochlorites, particularly sodium hypochlorite, are widely used for the purpose. Sodium hypochlorite, although recognized as an effective and relatively cheap bleaching agent, has certain inherent disadvantages. Because of its instability, it can be handled only as a dilute aqueous solution requiring bulky and inconvenient containers and having a limited shelf life. Hypochlorites also have a damaging effect on fabric tensile strength. Recently, organic nitrogen compounds containing nitrogen-bonded chlorine atoms in their structure have been offered for bleaching use, for example, trichloroisocyanuric acid, potassium dichloroisocyanurate, dichlorodimethylhydantoin, and related compounds. These have the advantage of being solids and therefore are capable of being formulated into solid bleaching compositions, bleaching cleansers, and the like. However, these materials are not entirely suitable for the purpose, having one or more of such disadvantages as poor dry stability, insufficient water solubility, or low bleaching efficiency.

Chlorine-liberating bleaches such as those described above also tend to attack the structure of many textile fibers, causing yellowing and a loss of tensile strength. This effect is particularly noticeable in fibers having nitrogen atoms associated with their structure; for example, silk, wool, synthetic polyamides, or fibers coated or impregnated with nitrogen-containing materials such as melamine resin-finished cotton.

It has now been found that many of the above-mentioned disadvantages are largely overcome or avoided by the use as bleaches of certain tetraalkyl ammonium perhalides. Most effective for the purpose are the perhalides having the structure $R_4NBr_nCl_{(3-n)}$, wherein each R is a lower alkyl radical containing 1–6 carbon atoms and n is an integer from one to three inclusive. The compounds included are therefore the tetraalkyl ammonium dichlorobromides, dibromochlorides, and tribromides. Most preferred, particularly on economic grounds, are the dichlorobromides. Compounds wherein at least three R's are methyl are advantageous because of their relatively higher water solubility.

The perhalide compounds described above have been found to be effective and advantageous bleaching agents when applied in water dispersion to various substances having undesirable and bleachable color or stain. Straw, wood pulp, paper stock, leather, various natural fibers such as cotton, silk, wool, and linen, and synthetic polyamide, polyester, and other like fibers may be treated by this process to remove natural or foreign discoloration.

These perhalides are crystalline solids which are stable while dry and they may be incorporated as bleaching components of various dry formulations for household and industrial use. The tetraalkyl ammonium perhalides are relatively soluble in water and, when so dissolved, readily liberate two atoms of halogen per molecule. Dichlorobromides liberate one atom each of chlorine and bromine while dibromochlorides and tribromides liberate two atoms of bromine.

These compounds have been found to have particular advantage in the bleaching of fabrics which have been treated with nitrogen-containing resins for crease resistance. Specifically, melamine resin-treated cotton may be bleached by these compounds with less yellowing and weakening of the fabric than is possible with the commonly used chlorine bleaches. These results are obtained along with bleaching efficiencies at least as high as those shown by chorine-liberating bleaches when used in equivalent halogen concentrations.

EXAMPLE 1

One liter portions of water in stainless steel beakers were heated to 130° F., the bleaching compounds to be tested were dissolved in the respective beakers of water, and the pH of each test solution was adjusted to 9–10 where necessary by the addition of tetrapotassium pyrophosphate. Bleaching efficiencies were measured at concentrations of 300 p.p.m. available halogen calculated as chlorine. Available halogen was determined by titration of iodine released from an acidified KI solution by a known quantity of perhalide. Three 5-inch squares of unbleached cotton sheeting were bleached for 10 minutes with agitation in each test solution, the cloths were rinsed 5 minutes in water, and they were pressed dry with a hand iron. The average reflectance of the three swatches of cotton sheeting as measured by a reflectometer was taken as a measure of bleach performance. The figures given are percentages based on a magnesium oxide block standard which is assigned a value of 100% reflectance.

Table I

Bleaching compound:	Average reflectance
Sodium hypochlorite	84.5
$(CH_3)_3C_2H_5NBrCl_2$	84.3
$(CH_3)_3C_2H_5NClBr_2$	85.0
$(CH_3)_3C_4H_9NBrCl_2$	84.2
$(CH_3)_4NBrCl_2$	84.3

EXAMPLE 2

In the manner described above, samples of white melamine resin-finished cotton print cloth were treated with various bleaching compounds and rinsed with water. These samples were dried in an electric dryer and inspected visually for yellowing. Table 2 lists data obtained at bleach concentrations of 300, 500, and 700 p.p.m. available halogen as chlorine.

Table II

Bleaching Compounds	Relative Yellowing		
	300 p.p.m. Cl_2	500 p.p.m. Cl_2	700 p.p.m. Cl_2
Sodium hypochlorite	Slight	Moderate	Heavy.
Potassium dichloroisocyanurate.	do	do	Moderate.
$(CH_3)_3C_2H_5NBrCl_2$	Very slight	Very slight	Very slight.
$(CH_3)_3C_2H_5NClBr_2$	do	do	Do.
$(CH_3)_3C_4H_9NBrCl_2$	do	do	Do.
$(CH_3)_4NBrCl_2$	do	do	Do.

EXAMPLE 3

By the procedure of Example 2, samples of white cotton print cloth and white melamine resin-finished cotton print cloth were treated with various bleaching compounds at 300 p.p.m. available halogen as chlorine, rinsed, and dried. The bleached cloths were subjected to tensile strength tests on a Baldwin-Tate-Emery load indicator using A.S.T.M. Grab Test conditions with 1¼ x 6 inch test pieces of fabric. The data obtained are listed in Table III.

Table III

Bleaching Compound	Tensile Strength, lbs.	
	Regular Cotton	Resin-finished Cotton
Sodium hypochlorite	40.3	27.6
Potassium dichloroisocyanurate	34.3	28.1
$(CH_3)_3C_2H_5NBrCl_2$	38.3	31.6
$(CH_3)_3C_2H_5NClBr_2$	41.2	34.9
$(CH_3)_3C_4H_9NBrCl_2$	37.5	33.5
$(CH_3)_4NBrCl_2$	40.8	33.0
Blank	51.3	33.8

The tetraalkyl ammonium perhalides are also advantageous in that they are effective bleaching agents in acidic solutions although best results are obtained at high pH levels, a pH of about 9–11 being preferred. Additionally, at both high and low pH, these compounds are not only efficient bleaches, but also show low redeposition of stain upon the bleached fabric. A further advantage of these perhalides lies in the biocidal free halogen which is liberated upon contact with water, thereby making these compounds disinfectants as well as bleaches.

I claim:

1. A process for bleaching natural and synthetic fibers which comprises applying to said fibers a water dispersion having dissolved therein an effective amount of a compound having the structure $R_4NBr_nCl_{(3-n)}$ wherein each R is a lower alkyl radical containing about 1–6 carbon atoms and n is an integer from one to three inclusive.

2. The process of claim 1 where in n is one.

3. The process of claim 2 wherein at least three of the R's are methyl radicals.

4. The process of claim 2 wherein the fiber bleached is melamine resin-finished cotton.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, after line 23, insert the following:

OTHER REFERENCES

Chattaway et al., J. Chem. Soc. (London) 123, Pages 654-62 (1923) through 17 Chem. Abstr. 1949 (1923).

Signed and sealed this 6th day of April 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
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