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MATERIAL TREATMENT

Irving E. Muskat, Akron, and George H. Cady,
Wadsworth, Ohio, assignors to Pittsburgh Plate
Glass Company, Allegheny County, Pa., a cor-
poration of Pennsylvania

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This invention relates to processes of bleaching fibrous materials. The use of chlorine and certain chlorine compounds as bleaching agents has long been known. While it has been very common to effect bleaching by means of hypochlorites of the alkali or alkaline earth metals, certain disadvantages arise from such a procedure. Alkaline hypochlorites of course contain substantial quantities of alkali and are therefore corrosive and tend to contaminate and to attack the material being treated to an undesirable degree. Bleaching with alkaline hypochlorites, in general, results in the contamination of the fibrous product with alkali or alkaline earth metal hydroxides and carbonates which must be removed before the treated product may be suitably sized. This necessitates considerable washing and consequent expenditure of time, labor and money. In addition, the alkaline hypochlorites, in general, contain substantial quantities of chlorates which are also corrosive and which attack the fibers being bleached. Furthermore, the rate of bleaching action of the alkaline hypochlorites is relatively low and as a result, considerable time is required to produce a suitably bleached product.

While chlorine water has been used to some extent as a bleaching agent, it has similar disadvantages. Chlorine water is highly corrosive due to the presence of large amounts of HCl therein. The use of this bleaching agent, in general, results in a severe attack upon the fibers and in considerable contamination thereof. Moreover, the solubility of chlorine in water is so low that suitable bleaching can be secured only after prolonged treatment for a considerable length of time. During treatment, further quantities of HCl are generated thereby, resulting in a corresponding decrease in bleaching power and an increase in the corrosiveness of the liquor. Thus, the use of chlorine water as a bleaching agent is unsuitable for many purposes.

Hypochlorous acid has been used to some extent for bleaching but, in general, this acid has been too unstable and the results obtained have been too irregular to be suitable for commercial processes. In accordance with our invention, we have discovered that HOCl may be used efficiently as a commercial bleaching agent under certain conditions. In the past, commercial HOCl contained substantial quantities of HCl, chlorine, chlorides, chlorates, bicarbonates, salts of the alkali or alkaline earth metals, etc., and we have determined that the undesirable results obtained from the use of this material in bleaching proc-

esses have been due to one or more of these impurities. We have found that excellent bleaching may be secured from use of aqueous solutions of HOCl which initially are substantially free of these impurities. Such solutions are comparatively very stable and require only a relatively short period of time to effect a satisfactory bleaching. Fibrous materials, such as rayon, cotton, silk, wood pulp, etc., may be bleached successfully with this agent.

HOCl as used in this process may be prepared by a convenient method which will insure the desired purity. We have found that extremely pure HOCl may be prepared by contacting water, which is substantially free from impurities, with chlorine monoxide. Ordinary tap water is generally suitable for this purpose. Other methods of making HOCl may also be found satisfactory.

The amount of chlorine monoxide per liter of water may be varied to some degree but, in general, a solution containing up to 20 per cent HOCl is found to be satisfactory. The chlorine monoxide used may be in the form of a pure gas if desired, but, in general, it is found preferable to treat water with a fluid containing small quantities of Cl₂O, from 1 to 25 per cent, the remainder of the fluid being made up of suitable diluents, such as carbon dioxide, nitrogen, helium, carbon tetrachloride, etc., but preferably free of contaminating impurities, such as hydrogen chloride, oxides of nitrogen, chlorine dioxide, etc. Substantial quantities of chlorine may be present in the chlorine monoxide-containing fluid since it is found that the chlorine monoxide dissolves in water so much more rapidly than chlorine that the HOCl solution prepared will contain only very minor quantities of HCl or chlorine. The temperature is preferably maintained at or below room temperature in order to avoid decomposition.

The HOCl may be prepared previous to the bleaching operation and used in the bleaching process before substantial decomposition of the HOCl occurs. This may be done, for example, by introducing chlorine monoxide into water and introducing the resultant HOCl solutions into the bleaching vat within a few minutes after formation. If desired, however, this acid may be generated in situ during the bleaching process by a convenient method as, for example, by contacting the aqueous slurry containing the fibers to be bleached with chlorine monoxide.

The process may be used to treat various fibrous products, such as wood pulp, silk, artificial silk fiber such as rayon, textile materials, etc., and

is especially effective in the bleaching of textiles without reduction of the tensile strength of the fibers.

In treatment of wood pulp, it may be used as a means of solubilizing noncellulosic incrustants, as a means of bleaching pulp from which the incrustants have been removed, or may be used to accomplish both of these results. The treatment may be used in conjunction with other bleaching processes which may precede or follow this process.

In bleaching wood pulp, or other fibrous materials, it has been found that it is desirable to dissolve the incrustants by treatment in an acid bleaching solution such as a substantially pure solution of HOCl strongly acidified with suitable acid, such as H₂SO₄, then to bleach in an alkaline solution such as a solution of an alkali metal or alkaline earth metal hypochlorite. This partially bleached product may then be thoroughly washed and treated in our high purity solution of HOCl.

The following examples illustrate the invention:

Example I.—A solution of hypochlorous acid containing 0.1% active Cl was prepared by introducing chlorine monoxide substantially free of HCl, chlorine dioxide or oxides of nitrogen, into a quantity of water at a temperature of 25° C. Skeins of viscose fibers were dipped in this solution at a temperature of 25–30° C. for a period of 6 minutes and were thereafter dipped in dilute sodium carbonate solution and thoroughly washed. The product was very white and the treatment exhibited no tenderizing action. When a similar process is carried out under the same conditions, using an alkaline hypochlorite solution of equivalent active chlorine content, several times the period of treatment herein used is required to secure an equivalent bleaching.

Example II.—A quantity of substantially pure HOCl solution was added to a 3 per cent aqueous suspension of kraft pulp in an amount sufficient to establish an available chlorine content of 0.3% and the pH was adjusted to 1.5 by addition of H₂SO₄. After 5 minutes, the slurry filtered, repulped and a 0.5% solution of calcium hypochlorite and vigorously agitated for 25 minutes. The resultant pulp was filtered, thoroughly washed and treated with 0.1% solution of substantially pure HOCl solution. The product, after washing, was extremely white and free from contamination.

Example III.—An aqueous slurry of pulp of 4 per cent containing 1 per cent lignin consistency was vigorously agitated and a quantity of a gas containing chlorine monoxide diluted with carbon dioxide was bubbled into the slurry. After 30 minutes, treatment was discontinued and the pulp obtained was white and free from lignin.

The concentration of the bleaching solution may be varied to some degree but, in general, will not exceed an available chlorine content of 1.2%. If desired, the HOCl solutions may be prepared in concentrated form (form 10–20% HOCl) and diluted to the desired concentration when used. By this method, we are able to obtain bleaching solutions which are very free from undesirable impurities since dilution of the concentrated solutions which themselves are substantially free from HCl, chlorates, chlorides, carbonates or alkali metal or alkaline earth metal salts, insures the production of solutions of HOCl

containing no appreciable quantities of these impurities.

During treatment of the fibers with HOCl, it may be found that the bleaching liquor becomes contaminated with certain impurities such as HCl, chlorine, chlorates, chlorides, etc. In order to avoid substantial accumulation of these substances, it may be desirable to replace a portion of the bleaching liquor with fresh HOCl continuously or from time to time. In this manner, we may maintain the bleach liquor substantially free from these impurities during the major portion of the treatment.

Although the invention has been described in connection with the specific embodiments of certain details thereof, it is not intended that they shall be regarded as limiting the scope of the invention except insofar as included in the accompanying claims.

We claim:

1. The process of bleaching fibrous materials which comprises treating a quantity of water with chlorine monoxide, which is substantially free of hydrochloric acid, chlorine dioxide and oxides of nitrogen in concentrations sufficient to produce a solution of hypochlorous acid and bleaching fibrous materials with this solution.

2. A process of bleaching fibrous materials which comprises immersing said materials in a body of water which is substantially free from the impurities, chlorine dioxide, hydrochloric acid and oxides of nitrogen and introducing chlorine monoxide which is substantially free from said impurities into said body of water.

3. The process of bleaching fibrous materials which comprises treating a quantity of water with a fluid comprising chlorine monoxide substantially free from hydrochloric acid, chlorine dioxide and oxides of nitrogen, and a gaseous diluent which is substantially inert to fibrous materials in concentrations sufficient to produce a solution of hypochlorous acid and bleaching fibrous materials with this solution.

4. A process of bleaching fibrous materials which comprises immersing said materials in a body of water which is substantially free from the impurities, chlorine dioxide, hydrochloric acid and oxides of nitrogen and introducing a fluid comprising chlorine monoxide which is substantially free from said impurities and a gaseous diluent which is substantially inert to fibrous materials into said body.

5. The process of claim 3 wherein the diluent is carbon dioxide.

6. The process of bleaching fibrous material which comprises immersing said materials in a body of water and introducing a gaseous mixture containing chlorine and chlorine monoxide which is substantially free from hydrochloric acid, chlorine dioxide and oxides of nitrogen into said body of water.

7. The process of bleaching fibrous materials which comprises treating a quantity of water with chlorine monoxide which is substantially free from chlorine dioxide, hydrochloric acid or oxides of nitrogen to produce a relatively concentrated solution of hypochlorous acid of relatively high purity, diluting this solution with water to form a more dilute solution of said acid of higher purity and bleaching fibrous materials with said solution before substantial decomposition of the solution can occur.

IRVING E. MUSKAT.
GEORGE H. CADY.