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PROCESS OF BLEACHING COTTON WITH HYDROGEN PEROXIDE BLEACH STABILIZED WITH CALCIUM OR MAGNESIUM ORTHOPHOSPHATE

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This invention relates to continuous bleaching of textile fabrics by the peroxide system.

It is well known in the textile industry to bleach running lengths of cotton fabrics and the like by passing the fabric through a solution of alkaline hydrogen peroxide, to store and steam the fabric for a limited period of time in a J box and to remove the fabric from the J box for subsequent washing, additional bleaching and/or subsequent treatments. The hydrogen peroxide used in these systems is usually stabilized with sodium silicate.

Sodium silicate has been chosen for stabilization primarily because it promotes more efficient peroxide bleaching of cotton than any other stabilizer heretofore known. The use of sodium silicate as a peroxide stabilizer has one costly drawback which has heretofore been regarded as a necessary evil, i. e., that the silicate forms some sort of complex deposit on the sides of the J box storage unit. This deposit is so pronounced that after about three eight-hour shifts of continuous operation, it begins to cause bruise marks on the fabrics being bleached. To avoid "seconds" caused by bruise marks, J boxes used for storage of fabrics bleached with sodium silicate stabilized peroxide have to be cleaned at regular intervals. In some plants this means that the entire bleaching range must be shut down once every three or four shifts so that the J boxes may be cleaned and polished.

It has now been found that the deposits heretofore experienced in continuous peroxide bleaching systems can be avoided without sacrifice of the desirable bleaching properties of the peroxide.

According to this invention, sodium silicate is completely eliminated from the bleaching system and the treating solution comprises peroxide, at least about 0.017 moles per liter of a water soluble orthophosphate, and a buffer which may be an alkali borate or an additional amount of the phosphate. The pH of these bleaching solutions is adjusted to from about pH 9 to pH 11.

Where the cotton being bleached has been previously kier boiled, to maintain the best bleaching conditions it is necessary to add a small amount of a salt of an alkali earth metal, preferably a calcium salt such as CaCl_2 . A similar safeguard may be required in those instances where the water is very soft.

The term "phosphate" as used in this specification means a salt of orthophosphoric acid (H_3PO_4) and not a pyrophosphate, metaphosphate, polymetaphosphate, hexametaphosphate, tripolyphosphate, tetraphosphate, etc. The latter compounds are inoperative in the process covered by this invention.

It has been found that cotton fabrics impregnated with a bleaching solution as described and then heated and stored hot in J-boxes as practiced in continuous peroxide bleaching are bleached very satisfactorily. This is very surprising in view of the fact that hydrogen peroxide in an alkaline solution containing orthophosphate has a low degree of stability on heating. It would therefore be expected that a large part of the peroxide applied to

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the fabric would be lost by decomposition and not usefully employed in bleaching. Contrary to expectations this is not the case, but the stability of the peroxide on the treated fabric is high and the bleaching results are excellent.

It is believed that the reason for this very unexpected behaviour is to be seen in the presence on the fabric of certain substances which in combination with the orthophosphate have a strong stabilizing effect on the hydrogen peroxide of the bleaching liquor. It is believed that these stabilizing substances are probably present as non-cellulosic impurities on raw cotton and still present on the fabric when it has been desized and is ready for bleaching. As to the nature of these stabilizing substances there is reason to believe that they consist of compounds of calcium and magnesium. It has been found that addition of small amounts of calcium salts to an alkaline solution of orthophosphate and peroxide, amounts sufficient to produce a slight precipitate of calcium phosphate, exercise a strong stabilizing effect on the peroxide so that only little decomposition of peroxide takes place even when these solutions are heated. The presence of a precipitate is essential as filtered solutions lose their stability.

Addition of 100 parts per million of calcium chloride, for instance, is sufficient to impart excellent stability to an alkaline peroxide solution containing orthophosphate. Magnesium salts have a similar effect. On the other hand, when a fabric sample is treated with dilute hydrochloric acid, and then rinsed thoroughly with distilled water, that treatment removes from the fabric all calcium and magnesium. Such fabric cannot be successfully bleached according to that form of this invention in which no metal salt is added. It remains yellow and full of moles while a similarly treated sample of the same fabric which had not undergone the acid treatment was bleached to a good white and was free of moles. The acid treatment which removed calcium and magnesium from the fabric had obviously an adverse effect on the bleaching process. These facts support the view that calcium and magnesium orthophosphates formed on the cloth are responsible for the unexpected result that alkaline peroxide solutions containing orthophosphates can be successfully used in the process described in this invention.

To assure uniformly good bleaching it is desirable to add about 0.02% calcium chloride to the treating solution, or similar amounts of other salts of alkaline earth metals.

In addition to the small amount of orthophosphates required for the above purposes, suitable buffers may be added. Such buffers are necessary to neutralize the acidic oxidation products formed during the bleaching process.

Orthophosphates themselves have good pH buffering properties, particularly at pH about 10.5 and higher and may be used alone when present in sufficient concentration. It is, however, to be understood that the presence of soluble orthophosphates at a minimum concentration of about 0.3% is an indispensable part of this invention, and required even if other buffers are present to control pH. This is shown in the following series where borax was used as a pH buffer. (It will be obvious that 0.3% of disodium orthophosphate duohydrate may also be stated as 0.017 mole per liter of a water soluble orthophosphate.)

Two series of specimens were made to determine the criticality of the concentration of orthophosphate. In both instances the formula used for the bleaching liquor was as follows:

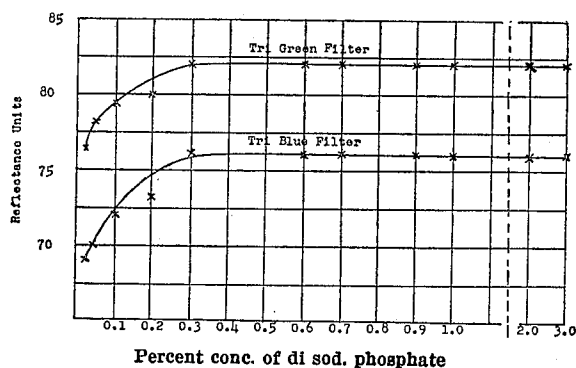
0.5% borax
0.02% calcium chloride
0.5% hydrogen peroxide
Sodium hydroxide and orthophosphate as indicated,

A desized cotton sheeting containing hardness of 1200 parts per million expressed as calcium carbonate was bleached in twelve samples of the above formula having 0.025, 0.050, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% respectively of disodium phosphate duohydrate. In each bleaching solution the pH was adjusted to 9.6 with sodium hydroxide. The samples were impregnated with the bleaching solution on a laboratory pad so as to take up their own weight of bleaching liquor. The samples were then enclosed in glass containers and thus substantially protected from losing water by evaporation. All samples were then heated at 90° C. for 1½ hours, rinsed and dried. The results of this experiment are shown in Graph I.

A second series was run in an identical manner using a desized cotton sheeting having a hardness of 3300 parts per million expressed as calcium carbonate. The results of this second series are set forth in Graph II.

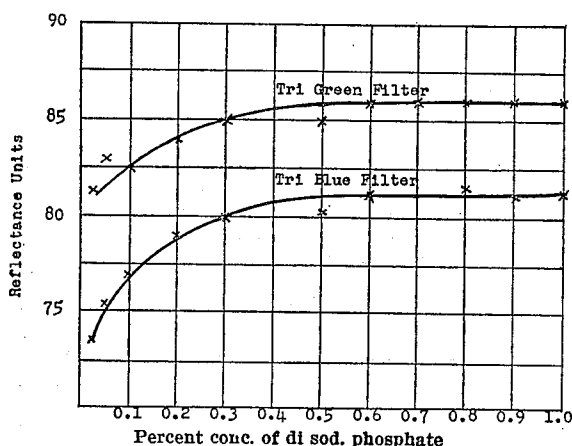
GRAPH I

Whiteness vs. phosphate concentration



GRAPH II

Whiteness vs. phosphate concentration



It is evident that a minimum concentration of about 0.3% disodium phosphate duohydrate was necessary to obtain the best possible whiteness with the amount of hydrogen peroxide used. At the pH 9.6 the orthophosphates have hardly any buffer action. The borate, and not the orthophosphates, are therefore the buffer in the series of bleaching tests described.

The phosphates have in the bleaching process here disclosed a particular beneficial function which cannot be explained as the function of an alkaline buffer.

The following are typical examples of the invention:

EXAMPLE I

A bleaching solution was prepared containing:

0.5% hydrogen peroxide
200 parts per million calcium chloride
2.0 disodium phosphate duohydrate

The pH was adjusted to 10.7 with sodium hydroxide and the mixture was agitated to keep the precipitated calcium orthophosphate suspended. This formula was fed to a conventional bleaching pad box and desized undyed cotton fabrics were bleached continuously on a conventional open width bleaching range for 3 shifts without stopping. At the end of the run, the storage J box was inspected and instead of the usual deposit, the walls of the J box appeared to have been polished even more highly by the passage of the fabric therethrough.

EXAMPLE II

A bleaching solution was made of the following formula:

15 .5% borax
1.35% trisodium phosphate dodecahydrate
0.25% disodium phosphate duohydrate
0.02% calcium chloride
20 0.5% hydrogen peroxide

The pH was adjusted to 9.6 with sodium hydroxide and the solution was continuously agitated to keep the calcium orthophosphate precipitate suspended. This slurry was fed into a conventional bleach pad box of a conventional rope bleaching range. Yarn dyed cotton plaids were continuously bleached for three 8-hour shifts. At the end of the three shifts, the storage J box was inspected and the walls of the box appeared to have been polished by the movement of the fabric. There was no deposit.

Fabric bleached according to Examples I and II were compared with otherwise identical fabrics bleached with silicate bleach according to conventional procedure on the same ranges. On the plaid fabrics, bleaching experts normally accustomed to evaluating degrees of whiteness by visual examination repeatedly identified the samples bleached in accordance with this invention as having a superior white, or an equivalent white.

The samples from Example II were also checked for bleeding and color running and it was found that there was considerably less damage to the colors than by conventional bleaching.

The silicate bleached plain fabric and the fabric bleached in accordance with Example I were both bleached to about the same degree of whiteness.

EXAMPLE III

A bleaching solution was prepared containing:

0.5% borax
1.0% sodium phosphate duohydrate
50 0.5% hydrogen peroxide

The solution was adjusted to pH 9.6 by addition of sodium hydroxide and fed into the saturator of a continuous bleaching range. Desized colored cotton fabrics were bleached on this range continuously for 5 days. No deposit had formed in the J box at the end of this period and the quality of the bleach was judged as good or better than the bleach usually obtained with similar fabrics when using the conventional silicate-peroxide bleaching method.

This invention has been written with particular reference to hydrogen peroxide, but it will be understood that it is also applicable to other peroxide-yielding materials which are useful in bleaching textiles, such as sodium perborate and the like.

I claim:

1. In the process of continuously bleaching cotton fabric wherein said fabric is continuously moved from a supply station to a storage J box and removed and the moving fabric is first impregnated with a bleaching concentration of stabilized hydrogen peroxide and thereafter steamed in the J box until the fabric is bleached, that improvement which comprises stabilizing said peroxide with a stabilizing amount of at least 0.017 mole per liter of orthophosphate ions in the presence of a stabilizing amount of at least about 100 parts per million of alkaline earth metal

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ions selected from the group consisting of calcium ions and magnesium ions, said ions forming stabilizing amounts of calcium and magnesium orthophosphate, the stabilized solution being buffered to from pH 9 to pH 11 with a buffering agent selected from the group consisting of alkali metal borates and alkali metal orthophosphates.

2. In the process of continuously bleaching cotton fabric wherein said fabric is continuously moved from a supply station to a storage J box and removed and the moving fabric is first impregnated with a bleaching concentration of stabilized hydrogen peroxide and thereafter steamed in the J box until the fabric is bleached, that improvement which comprises stabilizing said peroxide solely with a stabilizing amount of at least 0.017 mole per liter of sodium orthophosphate in the presence of a stabilizing amount of at least about 100 parts per million of alkaline earth metal ions selected from the group consisting of calcium ions and magnesium ions, said ions forming stabilizing amounts of calcium and magnesium orthophos-

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phate, the stabilized solution being buffered to from pH 9 to pH 11 with a buffering agent selected from the group consisting of alkali metal borates and alkali metal orthophosphates.

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