

2,740,689

PEROXIDE BLEACHING WITH POLYPHOSPHATES AND ALKALI SALT OF EDTAA

Bernard K. Easton, Kenmore, and William H. Kibbel, Jr., Buffalo, N. Y., assignors, by mesne assignments, to Food Machinery and Chemical Corporation, San Jose, Calif., a corporation of Delaware

No Drawing. Application April 26, 1952, Serial No. 284,644

3 Claims. (Cl. 8—111)

This invention pertains to a method of bleaching cotton textiles with hydrogen peroxide and more particularly to a novel method of steam-bleaching cotton textiles with hydrogen peroxide.

The art of bleaching cotton textiles with hydrogen peroxide has developed over the years in three clearly discernible stages. In the very beginning, bleaching in open containers was customary. A variety of vats, tubs, jigs and the like was used, ordinarily equipped with steam inlets or steam coils to permit heating the bleach bath. The literature of those days abounds with recipes for bleach bath compositions, which prescribed the use of hydrogen peroxide together with an activating alkali and stressed the need to prevent undue bath decomposition by the addition of stabilizing agents to the bath. Soap, glue, borax, phosphates, vegetable gums, starch and a host of others were recommended as suitable, but sodium silicate was suggested most frequently.

As practical experiences were gained and the various advantages of hydrogen peroxide bleaching were more clearly recognized, the desire arose to operate in equipment more suitable for large scale commercial bleaching operations than the use of a vat or winch or dye beck. This second stage of development is characterized by kier bleaching methods coming to the fore. Kiers were always standard equipment in bleacheries and it was only natural that one sought to adapt standard kieriing methods to hydrogen peroxide bleaching. With the help of suitable coatings applied to the inside of the kiers initial difficulties due to the decomposing effect of unprotected kiers on the hydrogen peroxide bath were soon overcome. Studies on bleach bath composition had already shown that of the many different bleach bath stabilizers used at one time or another sodium silicate was by far the best and its use became universal.

During this second stage of development much effort was expended in improving the technique of kier bleaching. Proper bleach bath circulation was found to be very important and a variety of kier constructions embodying a variety of bath-circulating devices appeared. The question of how to heat the bleach bath was finally resolved in favor of external heat exchangers to avoid diluting the bath with condensed steam. To obtain higher processing rates the caustic pretreatment, ordinarily required to prepare the goods for hydrogen peroxide bleaching, was in many instances carried out in the same kier which then served to carry out the bleaching treatment. This avoided the need to transfer the goods from a caustic prepare kier to the bleach kier, an operation requiring considerable time with larger units holding many thousands of pounds of cotton goods. A new set of difficulties arose, however, in this type of processing, because precautions became necessary to avoid carry-over of material solubilized during the caustic prepare into the bleaching step. Very careful washing cycles were worked out, often comprising a combination of water washes with hot soap or alkali washes, to permit nearly complete removal of the caustic prepare wastes from the goods. Because bleach-

ing efficiency was dependent on the thoroughness of the prepare, as well as on thoroughness of prepare waste removal, much study was devoted to the question of how to improve these operations. The effects of surface active agents on prepare and on prepare waste removal were investigated and a number of proprietary agents became more or less firmly established for use in caustic prepare formulae. The basic bleach bath composition, however, remained unchanged with hydrogen peroxide, sodium silicate and sometimes caustic soda as standard ingredients.

Although production rates in kier bleaching were higher than in the days of tub bleaching, they were still not high enough. Moreover, kier bleaching involves a substantial amount of costly manual labor.

As hydrogen peroxide bleaching of cotton goods became more and more commonplace, many efforts were made to raise production rates and lower production costs. These efforts successfully resulted in the development of modern steam bleaching processes, which represent the third stage of development of the art.

Modern steam bleaching ranges, the principles of which are given for example by Clark and Smolens Letters Patent of the United States 2,029,985 and Kauffmann and Shanley 2,353,615, are complicated pieces of machinery, involving not only specifically designed J-boxes as actual bleaching units, but much auxiliary equipment, such as saturators, washers, electronically controlled electric drives, metering devices for continuous feeding of chemicals and the like. Obviously, much ingenuity and engineering knowledge were required to promote the art to its present high level of efficiency.

This revolutionary change in bleaching methods, evolving slowly over many years and culminating in today's nearly automatic high capacity bleaching ranges, left only one thing more or less unchanged, namely the principle of using sodium silicate as bleach bath stabilizer. Although other stabilizers such as phosphates, were recommended off and on, commercial practice in the bleacheries of most countries of the world called for the use of sodium silicate as bleach bath stabilizer.

Yet, the use of sodium silicate as stabilizer for alkaline hydrogen peroxide bleach baths is connected with certain disadvantages. These disadvantages, to be described shortly, were of very little practical importance in the days of tub and kier bleaching. This is however not so in today's steam bleaching operations. As steam bleaching in continuous ranges became more widely accepted by the industry and practical experiences with such ranges were gained over the course of time, it became more and more obvious that sodium silicate, outstanding in many respects as bleach bath stabilizer, was responsible for certain difficulties experienced with steam bleached goods and also with steam bleaching equipment.

These difficulties are basically due to the fact that under certain conditions a silicic acid compound will precipitate from hydrogen peroxide bleach baths containing sodium silicate.

All practical bleaching operations, with the exception of continuous steam bleaching operations, are carried out at a fairly high liquor ratio. That is to say, the amount of goods treated is smaller, sometimes very much smaller, than the amount of liquor used to treat the goods. In tub bleaching, liquor ratios of 1:10 and even 1:20 are common, meaning that in such operations 1 lb. of goods will be treated with 10 or 20 lbs. of liquor. Because the goods are here immersed in an excess of bath liquor, bath concentration is for all practical purposes the same on the surface of the goods and in the body of the bath. Although heating of the bath to operating temperatures may involve a certain loss of water by evaporation, this loss and the subsequent change in bath concentration is negligible from a practical viewpoint and does not affect the

uniform distribution of chemical concentration in the bath and on the surface of the goods. In kier bleaching operations, smaller liquor ratios of about 1:4 are encountered. But here again excess liquor is present and here again chemical concentration is the same on the surface of the goods and in the body of the bath. As excess liquor is also present in all washing operations preceding or following the bleaching treatment proper, little or no danger exists that a silicic acid compound may be precipitated from the baths employed. Even if precipitation should occur, the precipitate will be suspended wholly or in part in the excess liquor present and carried away during washing operations.

The situation is very much different in steam bleaching operations. Here the goods to be bleached are impregnated with the bleach bath, not immersed in a bleach bath. The liquor ratio in steam bleaching is therefore very small and of the order of about 1:1, more or less. There is no excess liquor present and the goods carrying about their own weight in bleach liquor are subjected to bleaching temperatures of about 100° C. for times ranging from perhaps 40 minutes to one hour or more. Although initially chemical concentration on the surface of the goods and in the limited amount of liquor carried by them is the same, this relation changes under operating conditions, because chemical absorption cannot be disregarded anymore where relatively small quantities of liquor are involved. Moreover, the technique of steam bleaching is such that evaporation losses are not completely avoided in certain phases of the over-all bleaching process. In other words, conditions in steam bleaching operations are such, that concentration changes in the bleach liquor can take place to an extent large enough to cause precipitation of silicic acid compounds. If and when such precipitation occurs, insufficient liquor is present to permit the precipitate to remain wholly or partly suspended in the liquor and consequently any precipitate formed will become deposited on the goods and/or on certain parts of the equipment in contact with the liquor and/or the goods.

Silicic acid compounds, as deposited on the goods or on the equipment, are hard, insoluble and abrasive. If deposited on equipment parts with which the goods are in sliding contact, abrasions of the surface of the goods are apt to occur. If deposited on the goods, a harsh handle might result and, still more serious, the absorbency of the goods will be substantially lower in those places where such deposits have occurred. This causes most serious difficulties in subsequent dyeing operations, where non-uniform absorbency gives rise to uneven dyeings. Uneven dyeings will also result from the abrasion effects observed when the goods were in sliding contact with equipment parts on which silicic acid compounds had deposited. In some instances abrasion marks or deposits on the goods themselves may be so pronounced as to make even white finished goods commercially less acceptable and in severe cases abrasion may actually lead to thread breaks in the fabric.

All in all, the use of sodium silicate in hydrogen peroxide bleach baths, although perfectly satisfactory in high liquor ratio operations, is very much less satisfactory in low liquor ratio operations such as in steam bleaching, where its use may lead to serious defects in the goods due to the effects of silicic acid compounds which may become deposited on the goods and/or the equipment. These disadvantages of using sodium silicate in steam bleaching are very serious, notwithstanding the fact that the bleach effects obtained in terms of brightness of the bleached goods are very satisfactory.

Ever since the disadvantages connected with the use of sodium silicate in steam bleaching had been recognized, attempts have been made to replace this stabilizer. The only other compounds known from past disclosures to be generally useful bleach bath stabilizers for bleaching operations other than steam bleaching are the phosphates. It was therefore tried to use phosphates, particularly py-

rophosphates and polyphosphates, instead of sodium silicate in steam bleaching. The use of phosphates, under steam bleaching conditions was expected to avoid the danger of forming objectionable deposits on the goods or on the equipment. This was actually found to be the case. However, whereas phosphates could be used as bleach bath stabilizers in high liquor ratio operations, their performance in low liquor ratio steam bleaching operations was very unsatisfactory. Any commercial bleaching process, to be acceptable to the industry, must meet certain requirements. It is obviously not enough that a given process prevents abrasion and related damage to the goods. The goods must emerge from the bleaching range with a satisfactory degree of brightness and at the same time undue bath decomposition as well as chemical attack of the fiber substance, usually measured in terms of cuprammonium fluidity, has to be avoided. Moreover, uniformity of bleaching effects as obtained in repeated runs is also very important, that is to say that bleaching results obtainable with a given procedure must be predictable. It is in these respects that phosphates do not perform satisfactorily. If they are used instead of sodium silicate in steam bleaching operations, insufficient brightness, at least moderately severe fiber attack and lack of uniformity of bleaching results are observed. These facts, unacceptable to a commercial bleacher, are by no means offset by the fact that phosphates avoid formation of objectionable deposits.

It is an object of the present invention to provide an improved method of steam bleaching of cotton goods with hydrogen peroxide.

It is also an object of the present invention to provide an improved method of steam bleaching of cotton goods with hydrogen peroxide, which method permits uniformly high brightness to be obtained on the bleached goods, while avoiding objectionable chemical and/or mechanical fiber attack.

It is a further object of this invention to provide an improved method of steam bleaching of cotton goods with hydrogen peroxide using a phosphate as a bleach bath stabilizer.

We have found that the advantage of avoiding formation of objectionable deposits connected with the use of phosphates as bleach bath stabilizers in steam bleaching operations is fully maintained, while the disadvantage of low bath stability, low brightness, lack of uniformity in bleach results and chemical fiber attack are avoided, if the bleach bath used in such steam bleaching operations contains, aside from hydrogen peroxide as bleaching agent and alkali as activating agent, both a phosphate and a sequestering agent.

A commercially useful stabilizer must permit to obtain with a given bleach bath, containing hydrogen peroxide as bleaching agent and an alkali as activating agent, consistently high brightness, must prevent chemical fiber attack and undue bath decomposition and must not lead to the formation of objectionable deposits on the goods and/or the equipment. These requirements are not met by the use of phosphates alone nor by the use of sequestering agents alone, but they are met by the combined use of a phosphate and a sequestering agent.

Sequestering agents such as the sodium salt of ethylene diamine tetracetic acid are in themselves not bleach bath stabilizers. If a bleach bath is made up with hydrogen peroxide as the bleaching agent, and sodium hydroxide as the activating alkali, bleach bath decomposition at operating temperatures is impracticably high and is not reduced by the addition of a sequestering agent to the bath. This is shown by the following table which gives data on decomposition of a typical bleach bath at temperatures below those prevailing in steam bleaching, in presence of relatively small amounts of activating alkali and using relatively large amounts of ethylene diamine tetra-acetic acid, sodium salt. In the following examples this compound is listed as "tetra salt."

TABLE I

Bleach Bath Composition	Percent Loss of active oxygen in 2 hours at 85° C.
Hydrogen peroxide 3 g./liter.....	65
Sodium hydroxide 0.1 g./liter.....	
Hydrogen peroxide 3 g./liter.....	
Sodium hydroxide 0.1 g./liter.....	75
Tetra salt 1 g./liter.....	

Phosphates alone, when used to replace sodium silicate in steam bleaching formulas, do overcome the serious difficulties due to formation of deposits, such as encountered if silicates are used as bath stabilizers. To show this, a small scale continuous bleaching unit was set up, in which a continuous rope of cotton fabric moved continuously through a bleach bath as used in steam bleaching operations. A grid, composed of stainless steel rods, was installed above the vessel holding the bleach bath and the fabric rope was threaded through this grid in such a manner that it passed out of the bleach bath, through nip rolls, through the grid in close sliding contact with its rods and back into the bleach bath. To make test conditions more severe, heat lamps were installed above the grid, so that the rate of evaporation of bleach bath splashings, as they accumulated on the rods, was substantially increased over the rate of evaporation ordinarily encountered in commercial operations. The bleach bath in one case contained 0.8% hydrogen peroxide 35%, 1.1% sodium silicate and 0.1% sodium hydroxide, in the other case the bath contained 0.8% hydrogen peroxide 35% and 0.8% sodium tripolyphosphate. With the bath held at a temperature of about 40° C., the fabric rope was run continuously for 64 hours through the device in each case. After this time the stainless steel rods were heavily coated with a hard, rough deposit when running the bath containing sodium silicate, but had a smooth, shiny appearance free from deposits when running the bath containing the phosphate.

Although deposit formation is avoided when using phosphates instead of silicates in steam bleaching operations, the over-all performance of phosphates as bath stabilizers is unsatisfactory. It is only the combined use of a phosphate and a sequestering agent, which in accordance with our invention, provides bleach bath stabilization, satisfactory in every respect.

The following examples will serve to illustrate the principle of this invention as applied to the steam bleaching of cotton fabrics. It is, however, understood that the principle of this invention is equally applicable to the steam bleaching of other materials, provided only that such materials lend themselves to steam bleaching operations generally. Examples of such materials are cotton in other than fabric form, and mixed textiles generally in various physical forms.

In all the following examples one and the same type of cotton sheeting was used as the test material. It was prepared for bleaching by desizing, treating with a sodium hydroxide solution containing 3% NaOH based on the weight of the goods, washing, souring with a dilute acetic acid solution to remove any residual alkali, and washing again with water.

The cotton sheeting, fully prepared and ready for bleaching, showed an average brightness of 65.7 as determined by means of a Hunter Reflectometer, and showed an average fluidity of 1.8, as determined by means of a standard capillary viscometer. These average values were the result of 4 parallel tests.

The steam bleaching tests were carried out in every case by preparing the appropriate bleach bath, impregnating the cotton sheeting with that bath in such a manner that every 100 g. of sheeting carried 100 g. of bleach bath and then subjecting the cotton sheeting in bulk form

to a steam atmosphere at ordinary pressure for a period of 1 hour. Thereafter the goods were carefully washed with water, dried and tested for brightness and fluidity.

The bleach bath composition given in the examples is typical for commercial steam bleaching of cotton goods, where concentrations of hydrogen peroxide 35% of about 1% based on the weight of the goods are customary. The activating alkali, usually sodium hydroxide, may be introduced into the bleach bath by alkali carry-over from the preceding sodium hydroxide prepare treatment or may be added directly to the bleach bath, as in the examples given here. A certain minimum amount of alkali must be present to activate the bleach bath, but a substantial increase of this amount over about 0.1% NaOH based on the weight of the goods is not necessary and sometimes actually inadvisable.

In bleach bath compositions as ordinarily used in commercial steam bleaching of cotton goods, stabilizer combinations in the amounts indicated by the examples perform satisfactorily. Phosphates in amounts of approximately 1% based on the weight of the goods in combination with sequestering agents, such as ethylene diamine tetra-acetic acid, in amounts of approximately 0.05% based on the weight of the goods will give excellent results. These quantities of phosphate and sequestering agent should not be reduced substantially, as this might produce less satisfactory stabilizing effects, but even a substantial increase of these quantities is not accompanied by improved effects.

Example 1

A bleach bath was prepared containing 0.8% hydrogen peroxide 35%, 0.1% sodium hydroxide and 0.8% sodium tripolyphosphate, based on the weight of the goods. The prepared cotton sheeting was impregnated with this bleach bath so that every 100 g. of sheeting carried 100 g. of solution. The goods were then steamed for 1 hour, washed, dried and tested.

The results obtained in 32 repeat runs were averaged and gave a brightness average value of 79.8 and a fluidity average value of 9.90. The difference between the maximum and the minimum brightness value of all runs was 6.0 points.

Example 2

A bleach bath was prepared containing 0.8% hydrogen peroxide 35%, 0.1% sodium hydroxide, 0.8% sodium tripolyphosphate and in addition 0.05% tetra salt, which is the sodium salt of ethylene diamine tetra-acetic acid, based on the weight of the goods. The goods were treated as in Example 1.

The results obtained in 32 repeat runs were averaged and gave a brightness average value of 81.6 and a fluidity average value of 6.34. The difference between the maximum and the minimum brightness value of all runs was 5.5 points.

Example 3

To obtain a higher brightness level than obtained in Examples 1 and 2, a bleach bath was prepared containing 1% hydrogen peroxide 35%, 0.1% sodium hydroxide and 0.8% sodium tripolyphosphate, based on the weight of the goods. The goods were treated as in Example 1.

The results obtained in 20 repeat runs were averaged and gave a brightness average value of 84.0 and a fluidity average value of 8.5. The difference between the maximum and the minimum brightness value of all runs was 1.3 points.

Example 4

A bleach bath was prepared containing 1% hydrogen peroxide 35%, 0.1% sodium hydroxide, 0.8% sodium tripolyphosphate and in addition 0.05% tetra salt based on the weight of the goods. The goods were treated as in Example 1.

The results obtained in 20 repeat runs were averaged and gave a brightness average value of 85.4 and a fluidity average value of 6.9. The difference between the maximum and the minimum brightness value of all runs was 3.9 point.

The results of Examples 1 to 4 are summarized in the following Table II.

TABLE II

Ex- amples	Bright- ness Increase over un- bleached goods	Percent Improve- ment in bright- ness due to Seques- tering Agent	Bright- ness Range in points	Percent Improve- ment in Brightness Uniformity due to Seques- tering Agent	Fluid- ity values	Percent Improve- ment in F values due to Seques- tering Agent
1.-----	14.1		6.0		9.9	
2.-----	15.9	12.8	5.5	8.3	6.34	36
3.-----	18.3		1.3		8.5	
4.-----	19.7	17.0	0.9	31.0	6.9	19

These data, as summarized in Table II, indicate the substantial improvement in brightness uniformity and reduction of chemical fiber attack, this latter expressed in terms of fluidity values, which results from the incorporation of a sodium salt of ethylene diamine tetra-acetic acid in a bleach bath containing hydrogen peroxide as the bleaching agent, sodium hydroxide as the activating alkali and a phosphate as an in itself insufficient stabilizer. In accordance with the principle of this invention, peroxy-gen compounds liberating or forming hydrogen peroxide in aqueous solution may be used instead of hydrogen peroxide, for instance alkali metal peroxides, caustic alkalies other than sodium hydroxide, alkali metal carbonates or other conventional peroxide activating alkalies may be used instead of sodium hydroxide, polyphosphates generally may be used instead of sodium tripolyphosphate and soluble salts of ethylene diamine tetra-acetic acid other than a sodium salt may be used. This acid itself or equivalent sequestering agents may be used instead of a sodium salt of ethylene diamine tetra-acetic acid and in the alkaline environment will be present as a metallic salt. The important feature is the employment of a phosphate and sequestering agent jointly.

As outlined above the goods to be bleached are impregnated by any conventional means, such as by padding rolls or by immersion in the bleach solution and elimination of excess solution, so that the liquor ratio is from about 60% to about 125%, based on the weight of the goods. Generally the goods will contain about their own weight of solution and therefore be padded to 100%. The damp goods are then steamed by passage into and through a confined steaming zone. In the continuous treatment of goods by steaming the proper bleaching time at elevated temperature is obtained by the employment of a J-box wherein the goods are piled and subsequently passed slowly therethrough all as illustrated in the United

States Letters Patent previously mentioned or by equivalent apparatus.

The employment of the polyphosphate eliminated the deleterious deposits upon the chute and accompanying equipment associated with steam bleaching where sodium silicate is an ingredient of the alkaline peroxide bleach bath. The damage to the goods due to abrasion by reason of such deposits is thus overcome by this invention.

What is claimed is:

1. In the method of bleaching cellulosic fibers, which comprises impregnating the fibers with from 60% to 125% of an alkaline peroxide bleaching solution and then exposing the impregnated fibers to a steam atmosphere, the improvement which comprises impregnating the fibers in the absence of soluble silicate with an alkaline peroxide bleaching solution containing as essential ingredients a polyphosphate and an alkali salt of ethylene diamine tetra-acetic acid.

2. In the method of bleaching cellulosic fibers, which comprises impregnating the fibers with from 60% to 125% of an alkaline peroxide bleaching solution and then exposing the impregnated fibers to a steam atmosphere, the improvement which comprises impregnating the fibers in the absence of soluble silicate with an alkaline peroxide bleaching solution containing as essential ingredients sodium tripolyphosphate and a sodium salt of ethylene diamine tetra-acetic acid.

3. In the method of bleaching cellulosic fibers, which comprises impregnating the fibers with from 60% to 125% of an alkaline peroxide bleaching solution and then exposing the impregnated fibers to a steam atmosphere, the improvement which comprises impregnating the fibers in the absence of soluble silicate with an alkaline bleaching solution containing as essential ingredients hydrogen peroxide 35%, about 1%, sodium hydroxide, about 0.1%, sodium tripolyphosphate, about 1%, and sodium salt of ethylene diamine tetra-acetic acid, about 0.05%, based on the weight of the goods to be treated.

References Cited in the file of this patent

UNITED STATES PATENTS

2,012,462	Agthe	Aug. 27, 1935
2,168,181	Ulrich	Aug. 1, 1939
2,193,173	Jellinek	Mar. 12, 1940
2,283,141	Kauffmann	May 12, 1942
2,334,066	Campbell	Nov. 9, 1943

FOREIGN PATENTS

434,599	Great Britain	Sept. 5, 1935
721,317	Germany	June 2, 1942
811,938	France	Apr. 26, 1937

OTHER REFERENCES

- Jackman: "Chemistry of Laundry Materials," p. 81.
 "Versene," Technical Bulletin No. 1, copyright 1949,
 24 page booklet, p. 2 especially pertinent.