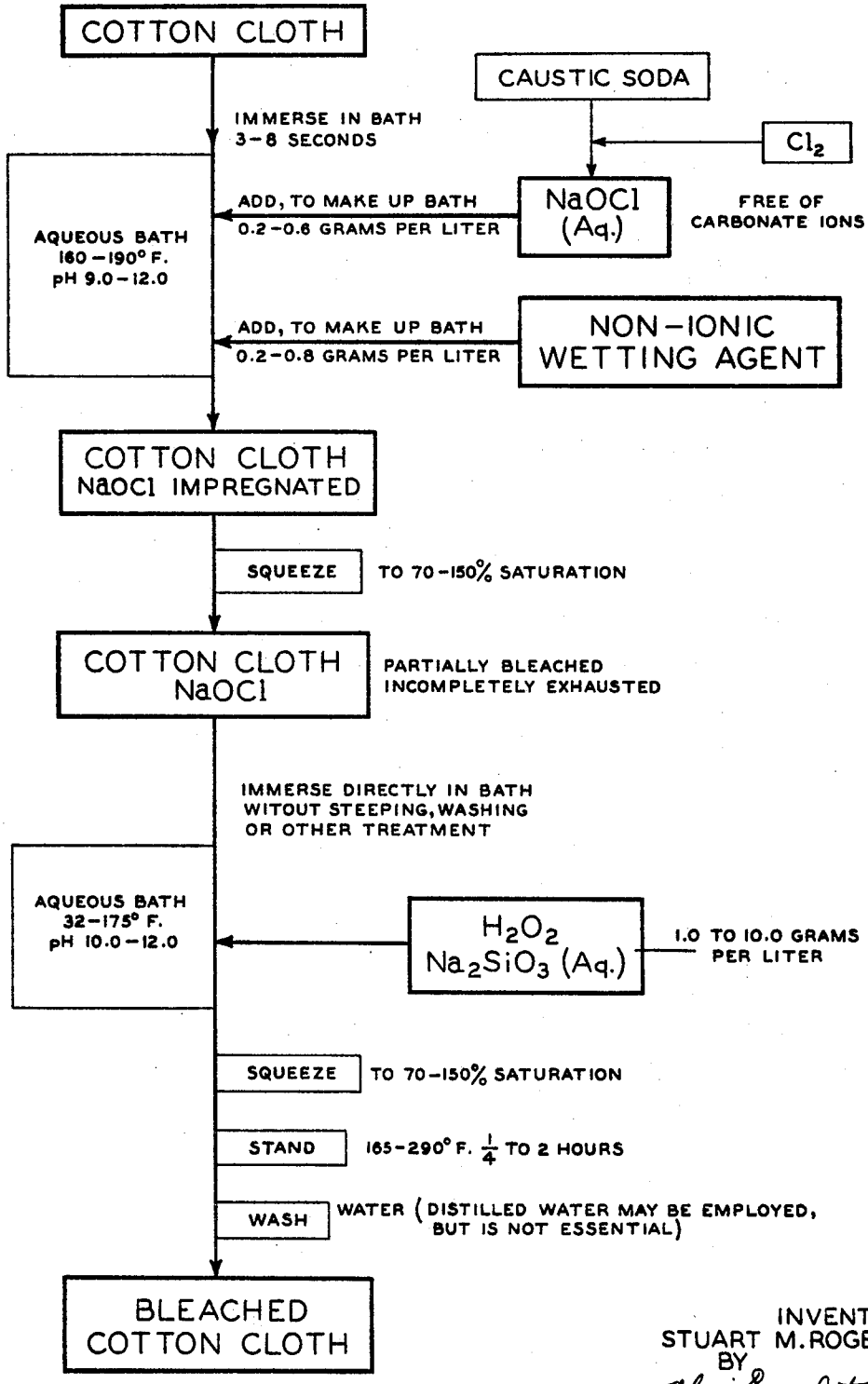
Aug. 9, 1966 S. M. ROGERS 3,265,462

HIGH-SPEED TWO-STAGE BLEACHING OF COTTON CLOTH

Filed Oct. 12, 1962



INVENTOR
STUART M. ROGERS
BY
Alvin Engelstein
ATTORNEY

United States Patent Office 3,265,462 Patented August 9, 1966

3,265,462

HIGH-SPEED TWO-STAGE BLEACHING OF COTTON CLOTH

Stuart M. Rogers, Syracuse, N.Y., assignor to Allied Chemical Corporation, New York, N.Y., a corporation of New York

Filed Oct. 12, 1962, Ser. No. 230,216
2 Claims. (Cl. 8—109)

This invention relates to bleaching of cotton textiles and more particularly to new and improved combined hypochlorite-hydrogen peroxide process adapted to produce bleached cotton cloth of superior properties at high speeds.

Until fairly recently single stage hydrogen peroxide bleaching had for a number of years been commonly employed in the textile industry. In my U.S.P. 2,903,-327, issued September 8, 1959, is described a process in which cotton cloth is treated first with hypochlorite and then with hydrogen peroxide. This two-stage process produces bleached cotton cloth of improved properties at lower cost over the previous conventional peroxide processes and has achieved substantial commercial success. In the subject process cotton cloth is immersed in hypochlorite solution at normal temperatures followed by squeezing and steeping of the hypochlorite impregnated cloth for a period of about 5 to 45 minutes in a J-box at normal temperatures. Bleaching of the cotton cloth in the second stage involves immersion in hydrogen peroxide solution at reagent concentrations substantially lower than that previously employed in single stage peroxide bleaching, followed by squeezing, steeping in a J-box, and washing of the bleached cotton cloth.

In view of the recognized practical utility of the subject process investigation was undertaken to find improvements and thus further enhance this type of bleaching. It was recognized that one area of possible improvement involved the required steeping operation in the J-box between the hypochlorite stage and the hydrogen peroxide stage. It was further recognized that if the steeping operation could be eliminated that high speed bleaching of the cotton cloth in the two stage process could be obtained. As the J-box is a large and expensive equipment item its elimination would also significantly reduce capital investment in the process. In order to accomplish this purpose it would, of course, be necessary to attain cloth at about the same condition of treatment on exit from the hypochlorite bath as previously obtained at the end of the 5–45 minute steeping operation in the J-box. Inasmuch as substantial bleaching has taken place at the end of the hypochlorite steeping in the subject two-stage operation several methods involving more intense hypochlorite treatment were tried in an effort to duplicate these results in the cloth obtained from hypochlorite solution. In the course of experimentation under varying conditions it was found that the desired result could not be attained or that problems related to fabric degradation in the hypochlorite liquid destroyed the practical utility of the operation. In some cases where high whiteness was obtained the other important properties of absorbency and fluidity were badly depreciated. It was also found in our investigation that a high temperature hypochlorite treatment favored bleaching but that the fabric degradation problem at high temperatures was most severe and difficult to overcome.

An object of the present invention is to provide a new and improved two-stage hypochlorite-hydrogen peroxide bleaching process for cotton cloth. Another object of the invention is to provide a high-speed two-stage hypochlorite-peroxide bleaching process in which the requirement of steeping the hypochlorite impregnated cloth and thus the J-box between the two stages is eliminated while still providing a cloth sufficiently treated that the reagent requirements in the hydrogen peroxide stage are reduced to at least the low levels possible in my prior U.S.P. 2,903,327. A further object is to provide such a process in which a high temperature first stage hypochlorite treatment is utilized without the danger of cloth degradation so that the process has practical utility, and by such process to still further produce with respect to the properties of the bleached cloth a product not only having superior whitness as in my prior process but also equivalent to and even improved over that process with respect to properties reflecting cloth degradation, i.e., absorbency and particularly fluidity. Other objects and advantages will be apparent from the following description.

In accordance with the invention, high-speed two-stage hypochlorite-hydrogen peroxide bleaching to produce cotton cloth of overall superior properties is accomplished by treating the cotton cloth in a sequential manner under carefully controlled conditions involving: (A) immersing the cotton cloth for a period of time from 3 to 8 seconds, preferably 4 to 6 seconds, in an aqueous solution containing the combination of 0.2–0.6, preferably 0.3–0.5, grams per liter sodium hypochlorite and 0.2–0.8, preferably 0.4–0.8, grams per liter of a non-ionic surface-active wetting agent at a temperature between 160–190° F., preferably 170–185° F., said aqueous solution having a pH value of about pH 9.0 to pH 12.0 and being substantially free of carbonate ions; (B) squeezing the cloth impregnated with the solution containing sodium hypochlorite and the non-ionic surface-active wetting agent to 70–150 percent, preferably 80–120 percent, saturation; (C) thereafter directly and without steeping or washing, immersing the cloth in hydrogen peroxide solution containing 1.0–10.0, preferably 3.0–5.0, grams per liter of sodium silicate as an additive and having a pH value of pH 10 to pH 12, preferably pH 10 to pH 11, at a temperature within the range of about 32–175° F., preferably 50–100° F.; (D) squeezing the cloth impregnated with the hydrogen peroxide solution to 70–150 percent, preferably 80–120 percent, saturation and maintaining the thus squeezed cloth at a temperature within the range of about 165–290° F., preferably within the range of 190–240° F., for a period of ¼–2 hours, preferably ¾–1½ hours; and (E) washing the thus treated cloth with water. The bleaching process of the present invention is highly advantageous, particularly in the following respects: (1) elimination of the steeping operation and the requirement of large and expensive retention equipment such as the J-box between the hypochlorite stage and the peroxide stage; (2) a two-stage hypochlorite-hydrogen peroxide bleaching process in which the cloth from the hypochlorite stage need only be squeezed before the hydrogen peroxide stage permitting direct and immediate transfer from the first stage to the second stage and thus providing high-speed processing; (3) a high temperature hypochlorite first stage in which not only substantial bleaching is rapidly accomplished but also one in which cloth degradation is not a problem

affecting practical operation; (4) in addition to elimination of the J-box, substantial economic benefit and low cost bleaching of cotton cloth are realized by low reagent requirements—the presence of the minor amounts of the non-ionic wetting agent in the cloth transferred to the second stage hydrogen peroxide treatment effecting even a further reduction in reagent requirements in that stage over my prior process of U.S.P. 2,903,327 and (5) the production of bleached cotton cloth of overall superior properties including high whiteness, high absorbency and low fluidity, with fluidity and absorbency values improved over those obtained by the above-referred to prior two-stage process.

The accompanying drawing diagrammatically illustrates the process of the present invention.

Preliminary to bleaching, the cotton cloth is prepared by singeing, desizing and caustic treatment as is conventional. It may be desirable to wash the fabric with hot water to remove impurities which adhere to the cloth prior to desizing. Desizing may be accomplished by treatment with dilute sulfuric acid and with a solution of enzymes. The desizing operation may be followed by water washing and then by caustic treatment to effect further removal of impurities from the cloth. The caustic treated cloth may then be washed and subjected to souring, which is the action of a very dilute solution of a mineral acid on the fabrics to neutralize residual caustic remaining in the fabrics and to dissolve foreign matter. In some instances, either the caustic treatment or souring, or both, may be dispensed with in preparing cloth for bleaching depending upon the nature of the impurities.

In carrying out the present invention the cotton cloth prepared for bleaching is first subjected to high temperature treatment in a hypochlorite saturator in the presence of a non-ionic wetting agent and under carefully controlled conditions which not only permit the production of cotton cloth of superior properties but which also treat the cloth to a substantial extent permitting completion of the bleaching in the second hydrogen peroxide stage at low reagent concentrations. In the hypochlorite saturator a bath temperature of at least 160° F. is required, while the preferred temperatures of about 170–185° F. give the best results. Temperatures substantially above about 190° F. tend to deleteriously effect quality of the bleached cloth. The cotton cloth in the presence of the non-ionic wetting agent rapidly reaches the desired level of treatment during an immersion time of only 3 to 8 seconds permitting not only high-speed operation but also contributing to the production of cotton cloth of exceptionally high quality. A low concentration of hypochlorite is particularly important. At the high temperatures of operation in the presence of the non-ionic wetting agent the avoidance of a hypochlorite concentration in excess of 0.6 gram per liter is most important permitting practical operation of the process and avoidance of cloth degradation problems. The desired level of treatment in the first stage is readily obtained with as little as 0.2 gram per liter sodium hypochlorite. The preferred hypochlorite concentration is 0.3–0.5 gram per liter. The presence in the hypochlorite bath of ions other than those derived from sodium hypochlorite itself is undesirable at the high temperature operating conditions of the process where their increased activity has an adverse effect. The use of the non-ionic wetting agents which are fully soluble in water without ionization also has the advantage of avoiding introduction of contaminants such as sulfate and other ions as is common with other surface active materials. The cationic and anionic surface active agents have been found not to give the desirable results obtained with the non-ionic agents. The presence of carbonate ions has been found to adversely affect not only absorbency of the bleached cloth but also tending to cause absorption of silicate in the second stage peroxide treatment. Consequently, the use of soda ash or other salts as is common in treating with hypochlorite is avoided and the sodium hypochlorite used in the saturator prepared by direct chlorination of caustic soda.

Another important feature of the invention is the non-ionic wetting agent which not only permits rapid, uniform action of the hypochlorite but which also has been found to have a beneficial effect on properties of the bleached cotton cloth, particularly the properties of absorbency and fluidity. The preferred non-ionic wetting agents are the polyoxyethylene ethers of the higher alcohols and higher alkyl phenols. These materials may be prepared, for example, by the reaction of the alcohol or alkyl phenol with ethylene oxide at temperatures of about 120–200° C. in the presence of an alkaline catalyst. The higher alcohols and higher alkyl phenols used should have at least 5 carbon atoms in the alkyl portion of the compound, preferably 6–12 carbon atoms. The number of moles of ethylene oxide added during the reaction to make-up the polyoxyethylene chain portion of the product should be about 6–15 moles, preferably about 8–12 moles. The more preferred non-ionic agents are the polyoxyethylene ethers of the higher alkyl phenols containing 7–10 carbon atoms in the alkyl group and about 8–12 ethylene ether groups. Examples of the more preferred non-ionic agents include octyl phenyl polyethoxy ethanol, diisobutyl phenyl polyethoxy ethanol and isooctyl phenyl polyethoxy ethanol. Isooctyl phenyl polyethoxy ethanol may be obtained commercially from the Rohm and Haas Chemical Company as "Triton" N–100. A concentration of about 0.2 gram per liter of the non-ionic wetting agent is required in the hypochlorite liquor to be effective while concentrations substantially in excess of about 0.8 gram per liter offer no additional advantage and are impractical from an economic standpoint. The preferred concentration of the non-ionic material is about 0.4–0.8 gram per liter.

On removal from the hypochlorite saturator the cloth is squeezed to a dampened condition, desirably about 100 percent liquor saturation, i.e., a cloth-liquor ratio of about 1:1. The cloth is then ready for second stage treatment in the hydrogen peroxide bath where it is transferred directly without steeping, washing, or other treatment. The direct transfer of the squeezed cloth into the hydrogen peroxide bath is another feature of particular importance. The residual hypochlorite in the cloth carried over into the hydrogen peroxide bath appears to impart desirable properties to the finished cloth, and its neutralization by the peroxide liberates oxygen which is beneficial in the bleaching. Similarly, the retention of the residual non-ionic wetting agent facilitates the bleaching action by the peroxide contributing to the improved properties of the bleached cloth and enabling operation with still lower concentrations in the peroxide bath.

The cloth is introduced into the hydrogen peroxide bath where the concentration of hydrogen peroxide is maintained at 0.5–10.0, preferably 1.0–5.0, grams per liter. Sodium silicate as an additive controlling the release of oxygen is present in the bath in an amount of about 1.0–10.0, preferably 3.0–5.0, grams per liter. The concentration of hydrogen peroxide, the amount of sodium silicate and the temperature of the hydrogen peroxide solution may be varied over a considerable range since the sensitivity of the cloth is much lower with hydrogen peroxide than with sodium hypochlorite. The cloth need be immersed in the hydrogen peroxide bath only for sufficient length of time to saturate it, usually a matter of minutes. The wet cloth is squeezed to approximately 100 percent liquor saturation and passed to a J-box where it is heated to a temperature of approximately 212° F. by direct or indirect contact with steam for a sufficient length of time to effect the desired bleaching, usually of the order of between ½ to 1½ hours. The thus treated cloth is washed with water.

The whiteness of bleached cloth can be determined on a General Electric reflectometer with a blue filter. The results obtained are expressed as percentage reflectance as compared with reflectance of magnesium carbonate. A whiteness of 86 percent or higher is considered good for medium weight fabric.

The determination of the fluidity of cellulose dissolved in cuprammonium hydroxide solution is a very sensitive and accurate method for measuring the effect of bleaching upon cotton. It is particularly effective in measuring the modification or degradation of the cellulose fiber due to chemical processing and is largely independent of the fabric construction. This is a very useful test since the modification or degradation can be used to predict the effect of chemical treatments on the tensile strength of fabrics and their wearing qualities. Fluidity values are measured in rhes (reciprocal poises). Values above 6 indicate degradation of the cloth fibers. Values below 4 indicate superior fiber strength.

The absorbency of the fabric is tested by fastening ½ inch strips, without stretching, between prongs projecting from the edges of two discs, spaced about 6 inches apart by means of a supporting rod passing through the center of each disc. There are enough prongs so that several samples may be tested at one time. With the samples in place, the whole assembly is inserted in a vertical glass cylinder containing 1–1½ inches of distilled water. A stop watch is started simultaneously with this operation and at the end of five minutes the height of the water absorption is measured by means of a transparent scale attached to the outside of the cylinder by flexible bands. The zero point is adjusted to the water level. Each 1/16 inch rise of water in the fabric denotes one point of absorbency. The test is conducted at 70° F. with a relative humidity of 65 percent on conditioned fabric. Absorbencies are taken on both warp and filling of the cloth and averaged. An absorbency of 25–30 is acceptable and an absorbency above 30 is considered excellent.

As is well-known, the difficulty in bleaching lies not with obtaining a high value with respect to one of the properties of bleached cloth, but with respect to all properties. A brightness value of 86 is not uncommon in the bleaching of medium weight cotton fabrics with hydrogen peroxide. In order to obtain a bleached cloth of commercial quality it is particularly required that absorbency also be high and that fluidity be low. Cotton bleached cloth obtained under the highly specific controlled conditions of the present invention not only improves the economics of operation but also the properties of absorbency and fluidity of the bleached cloth while brightness remains at a high level, as will be evident from the following example.

EXAMPLE 1

Cotton cloth of 80 x 80 thread count, 4.00 yards per pound weight, was prepared for bleaching by singeing, desizing, caustic treatment and washing in the conventional manner.

A 5" x 7" sample of the prepared cloth was wet-out by immersing with mild agitation in an aqueous solution maintained at a temperature of 180° F. and containing 0.5 g.p.l. sodium hypochlorite and 0.75 g.p.l. "Triton" N–100 (isooctyl phenyl polyethoxy ethanol). Total immersion time in the hypochlorite solution was about 5 seconds. The hypochlorite solution had a pH of about pH 10.5. The cloth removed from the hypochlorite liquor was squeezed to about 120 percent saturation and without washing or other treatment was passed immediately into an aqueous hydrogen peroxide solution containing 1.68 g.p.l. hydrogen peroxide and 8.5 g.p.l. sodium silicate. The peroxide solution had a pH of about pH 10.8. Retention time in the peroxide liquor which was at room temperature was about one minute. The saturated cloth removed from the peroxide liquor was squeezed to about 120 percent liquor saturation and allowed to stand for one hour at a temperature of about 212° F. which was maintained by indirect heating. The bleached cloth was then washed ten times in lukewarm water, pressed dry between blotters, pressed again between fresh blotters at 600 p.s.i. for about 30 seconds, and dried on a paper sheet drier for about 10 minutes. The results obtained are summarized below in Table I:

Table I

Cloth properties:	Example 1
Absorbency	44.0
Fluidity	2.29
Brightness	87.7

From the above data, it will be evident that the cotton cloth bleached in accordance with the present invention is of particularly high quality based on all properties desired in the cloth. Specifically, the brightness of the cloth attained a high level of 87.7 or greater than that obtained with straight peroxide bleaching. Of particular importance, the absorbency of the cloth attained a high value of 44 or greater than that obtained by straight peroxide bleaching or the two-stage hypochlorite-peroxide process of U.S.P. 2,903,327. Although totally unexpected in view of the high temperature hypochlorite treatment fluidity of the cloth bleached in accordance with the invention was reduced to a substantially lower level of 2.29 indicating an exceptionally high quality cloth and improvement over both the conventional peroxide bleaching and my prior two-stage process. These results were attained during a short 5 second hypochlorite treatment with as little as ⅓ the concentration of hypochlorite previously employed in two-stage hypochlorite-peroxide treatment and with about ½ the normal concentrations of peroxide and silicate conventionally employed in straight peroxide treatment.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

I claim:

1. A process of bleaching to produce cotton cloth of high absorbency, high whiteness and low fluidity which comprises: (A) treating cotton cloth in a sequential manner by immersing the cotton cloth for a period of time from 3 seconds to 8 seconds in an aqueous solution containing the combination of 0.2–0.6 gram per liter sodium hypochlorite and 0.2–0.8 gram per liter of a non-ionic surface-active wetting agent at a temperature between 160–190° F., said aqueous solution having a pH value of about pH 9.0 to pH 12.0 and being substantially free of carbonate ions; (B) squeezing the cloth impregnated with the solution containing the sodium hypochlorite and the non-ionic surface-active wetting agent to 70–150 percent saturation; (C) thereafter directly and without steeping immersing the cloth in hydrogen peroxide solution containing 1.0–10.0 grams per liter of sodium silicate as an additive and having a pH value of pH 10 to pH 12 at a temperature within the range of about 32–175° F.; (D) squeezing the cloth impregnated with the hydrogen peroxide solution to 70–150 percent saturation and maintaining the thus squeezed cloth at a temperature within the range of about 165–290° F. for a period of ¼ hour to 2 hours; and (E) washing the thus treated cloth with water.

2. A process of bleaching to produce cotton cloth of high absorbency, high whiteness and low fluidity which comprises: (A) treating cotton cloth in a sequential manner by immersing the cotton cloth for a period of time from 4 to 6 seconds in an aqueous solution containing the combination of 0.3–0.5 gram per liter sodium hypochlorite and 0.4–0.8 gram per liter of a non-ionic surface-active wetting agent at a temperature between 170–185° F., said aqueous solution having a pH value of about

pH 10.0 to pH 11.5 and being substantially free of carbonate ions; (B) squeezing the cloth impregnated with the sodium hypochlorite solution containing the non-ionic surface-active wetting agent to 80–120 percent saturation; (C) thereafter directly and without steeping immersing the cloth in hydrogen peroxide solution containing 3 to 5 grams per liter of sodium silicate as an additive and having a pH value of pH 10 to pH 11 at a temperature within the range of about 50–100° F.; (D) squeezing the cloth impregnated with the hydrogen peroxide solution to 80–120 percent saturation and maintaining the thus squeezed cloth at a temperature within the range of

about 190–245° F. for a period of ¾ hour to 1½ hours; and (E) washing the thus treated cloth with water.

References Cited by the Examiner

UNITED STATES PATENTS

1,908,481	5/1933	Kaufmann	8—109
2,048,991	7/1936	Butz et al.	8—109
2,903,327	8/1959	Rogers	8—109

NORMAN G. TORCHIN, *Primary Examiner.*

H. WOLMAN, *Assistant Examiner.*