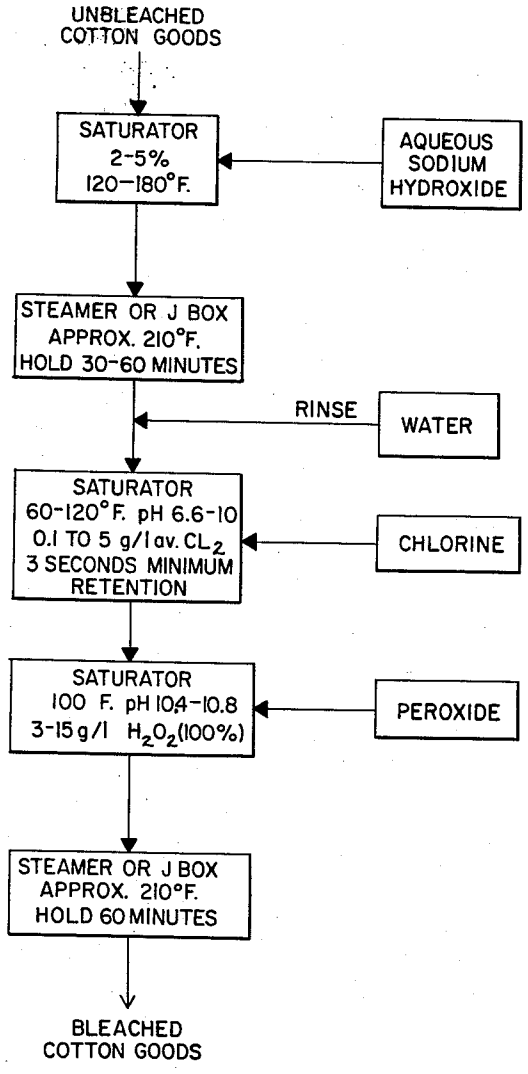
8-109 SR SEARCH ROOM
FIP8309 OR 3,077,372

Feb. 12, 1963 H. G. SMOLENS ETAL 3,077,372

SODIUM HYDROXIDE AND CHLORINE FOR IN SITU HYPOCHLORITE FORMATION IN PRETREATMENT OF COTTON IN PEROXIDIC BLEACHING

Filed Dec. 24, 1959



INVENTORS.
HARRY G. SMOLENS
OLIVER S. SPROUT, JR.

BY Robert G. Danehower
ATTORNEY

United States Patent Office 3,077,372 Patented Feb. 12, 1963

3,077,372

SODIUM HYDROXIDE AND CHLORINE FOR IN SITU HYPOCHLORITE FORMATION IN PRETREATMENT OF COTTON IN PEROXIDIC BLEACHING

Harry G. Smolens, Narberth, Oliver S. Sprout, Jr., North Hills, and Victor C. Lane, Fort Washington, Pa., assignors to Pennsalt Chemicals Corporation, Philadelphia, Pa., a corporation of Pennsylvania

Filed Dec. 24, 1959, Ser. No. 861,778
4 Claims. (Cl. 8—109)

This invention is directed to the continuous bleaching of cotton goods with hydrogen peroxide. More particularly, this invention relates to a process wherein alkaline residues accompanying cotton goods from a prior treatment are utilized to provide a bleaching composition which supplements the peroxide bleaching.

Fibers of cellulosic orgin such as cotton are customarily refined towards the end of the production operation by a series of processes which usually include scouring with caustic alkali and bleaching with hydrogen peroxide. The caustic alkali is used for removing fats and waxes. The treatment with the caustic alkali may leave the cotton discolored and bleaching operations are required for the finished goods, particularly where whiteness is desired.

As is well known in the art, it is extremely difficult to remove the caustic alkali from the cloth by washing operations, and it is believed by some people that the caustic soda chemically combines with the cotton. The sodium hydroxide is carried along to the subsequent bleaching operation unless measures are taken to secure its removal. It is necessary to prevent the carry-over of the residual alkali into the bleaching operation because of the detrimental effect of the caustic alkali on the peroxide solution. The securing of practical and economical ways of removing the residual caustic alkali from the cloth and thus preventing it from contaminating the peroxide bleach has been a problem of great concern to cloth manufacturers for many, many years.

Since hydrogen peroxide is an expensive treating agent in the processing of cotton cloth, any improvement in cloth processing which results in a reduction in the amount of hydrogen peroxide used effects important savings in the cost of processing the goods.

As the cotton leaves the caustic alkali saturator and steamer, it normally passes through washing operations in which the cloth is washed with hot water. These water washing operations remove most of the caustic alkali but fail to reduce the residual alkalinity in the cotton goods below about 0.5% to 0.05% by weight of the cloth. If excessive amounts of this residual caustic alkali are carried into the hydrogen peroxide saturator, the increased alkalinity of the hydrogen peroxide will either cause an excessive decomposition of the hydrogen peroxide or will render it unsuitable for use.

As is well known in the art, the peroxide solution used for bleaching cotton goods is not a simple solution of hydrogen peroxide but a complex mixture in which a number of additives are introduced with the peroxide in order to increase its stability. One of these additives is sodium silicate which is an alkaline material. Thus, if alkali is being introduced into the peroxide by the cloth itself, there will be an excess of alkali which will interfere with the action of the sodium silicate in the peroxide solution or the high alkalinity will preclude the addition of the silicate.

The residual alkali can be controlled by the addition of acid, but cloth processors generally do not correct for the carry over of the alkali into the peroxide because the neutralization with acid introduces complications of additional equipment, exact control procedures and cost of the acid itself. These complications arising from the use

of acid neutralization cost more than the savings to be obtained in consumption of peroxide by preventing alkali carry over.

For example, sulfuric or phosphoric acid will control the carry over of alkali with the cloth as shown in U.S. 2,602,723. This process requires additional equipment such as an acid saturator, J box, two additional water washers and squeeze rollers.

Another serious difficulty encountered in a souring operation with an acid is that extreme precautions must be taken to insure that the acid concentration does not exceed the desired limit or considerable degradation of the cloth will take place. In effect, this means that careful control procedures must be adhered to in order to insure that the acid concentration in the acid saturator does not exceed desirable limits.

We have now discovered a very simple process which removes the residual caustic alkali from the cotton cloth thereby materially decreasing the consumption of hydrogen peroxide. Moreover, these savings are effected without sacrificing any bleaching action by reduced consumption of hydrogen peroxide.

We have discovered that the residual caustic alkali in the cotton goods can be chlorinated with chlorine in aqueous solution continuously under substantially neutral conditions. Following the neutralization of the residual caustic alkali by passing the cloth through an aqueous solution in which chlorine is introduced, the cloth is then directed to the normal peroxide bleaching operation.

Since the bath in which chlorine is being introduced to neutralize the alkali is operated under substantially neutral conditions, it is not necessary to wash the goods after it emerges from the chlorinator. The cloth then goes directly to the peroxide bleaching operation and the absence of the residual caustic alkali in the cloth permits the hydrogen peroxide to be utilized to its fullest advantage under the proper conditions of alkalinity established for its use. Since chlorine is an inexpensive processing material, and since so little of it is required to neutralize the caustic alkali in the cloth, our novel process provides an inexpensive means for eliminating the difficulties attendant upon the carry over the caustic alkali to the peroxide fininshing stage.

An important advantage in using an aqueous chlorine solution to effect removal of the residual alkali is that the alkali itself is converted into a bleaching material by the reaction of it with the chlorine in aqueous solution. The chlorine and caustic alkali in water combine to form sodium hypochlorite which is a well-known bleaching agent. We have also discovered that by operating at substantially neutral conditions, that is at a pH of 6.6 to 7.4, we do not require that the cloth lay over in a J box for reaction. Alternatively, the chlorinator can operate under alkaline pH conditions in the range of 7.4 to 10.0.

In the practice of our invention the chlorine gas passes into a chlorinator filled with water simultaneously with the passage of the cloth into the water. The alkali entering with the cloth is continuously reacted with the chlorine with the production of hypochlorite. The pH of the chlorinator is preferably controlled at essentially a neutral pH thus providing the conditions most suited for instantaneous bleaching.

Another advantage of our process is that the hypochlorite bleach solution formed by the reaction of chlorine gas with the retained alkalinity in the cloth bleaches certain types of stains in the cotton not easily bleached by peroxide. Moreover, the bleaching accomplished by the hypochlorite is effected at practically no cost because it is prepared from a material which would normally be wasted from the process.

Cotton cloth goods, today, are processed in a contin-

uous manner. Generally, the cloth speed varies from about 100 yards per minute for open cloth bleaching to 300 yards per minute for rope bleaching. A normal finishing operation for cotton goods comprises, first, a water wash at a temperature of from 60 to 120° F. The hot water washing will remove some impurities from the cloth and assist in the removal of foreign particles adhering to the goods. After the water washing operation, the cloth is directed into a desizing bath wherein the cloth is exposed to the action of enzymes. After the desizing treatment, the cloth is moved into hot water washers to remove excess enzymes and to effect removal of the impurities produced by the enzyme treatment.

The goods then move into a caustic alkali saturator. The caustic solution is generally within the range of 2 to 5% and is held at a temperature of about 120 to 180° F. Following saturation with the sodium hydroxide sufficient time is allowed for the caustic to act upon the goods, usually in a J box, after which the cloth moves into several water washing stages to remove the caustic alkali and to effect solution and removal of the impurities which have been rendered by the sodium hydroxide. Squeeze rollers following the caustic saturator and following each washer assist in the removal of the excess carry over of liquid from one stage to the next.

Even with repeated washings with hot water at temperatures up to 200° F., it has been impossible to remove the alkali from the cloth below a value of about 0.5% to 0.05% by weight. The extensive washing will not remove all of the caustic soda from the cloth, and the pH of the last washing tank will vary from 9 to 11 depending upon whether copious amounts of water are used. This residual caustic interferes with bleaching and promotes decomposition of hydrogen peroxide.

The apparatus in which we effect the neutralization of the residual caustic alkali may conveniently be similar to that in which the caustic saturation is accomplished with some modification to accommodate the introduction of gaseous chlorine. Normlly, the gaseous chlorine is introduced at the bottom of the saturator through a diffuser such as a ceramic diffusing plate. No agitation is necessary in the saturator since the rapid movement of cloth through it accomplishes agitation of the liquid. Occasionally some water may be added to keep the chlorinator full, but normally, the water leaving the chlorinator is made up by that coming into the chlorinator with the cloth.

The most effective means of controlling the chlorine addition is to provide a pH controller in the chlorinator and have it regulate the introduction of the chlorine. It is necessary that the aqueous chlorinator be maintained within a pH of 6.6 to 7.4 for neutral bleaching or within the range of 7.4 to 10.0 for alkaline bleaching. The neutral pH range is preferred for rapid bleaching and elimination of holdover of the cloth in a J box for 20 to 40 minutes. If the cloth is saturated with the hypochlorite at a pH within the range of about 6.6 to 7.4, then the bleaching will take place within a matter of a few seconds. However, if the pH is allowed to rise to within the range of about 7.4 to 10.0, then the bleaching action is considerably slowed down and as long as 40 minutes may be required to obtain bleaching from the hypochlorite solution. Bleaching at a pH below 6.6 must be avoided because of the release of noxious chlorine containing vapors from the solution.

A pH control instrument such as a Brown-Beckman controller actuating the chlorine feed valve is a most desirable way to maintain the chlorinator at the desired pH. If the pH arises above the set point, that is, above 8.5 for alkaline bleaching, then the controller opens the chlorine inlet valve to admit the chlorine at a faster rate and the pH shortly thereafter is lowered. If the pH goes below 8.5, then the chlorine feed rate is decreased until the bath is again operating at the desired pH. This type of operation is very easy to accomplish with a continuous cloth feed and with a fairly uniform amount of retained alkalinity in the cloth.

In the chlorinator a low temperature is desired in order to maintain the chlorine in solution. Generally, the chlorinator bath will operate within a temperature range between 60 and 120° F. The preferred temperature is between 90 and 100° F. within which range an adequate amount of chlorine is maintained in solution, and the chlorine reacts rapidly with the incoming sodium hydroxide in the cloth.

It is necessary that the aqueous chlorinator be sized so that the cloth has a retention time of at least 3 seconds in the chlorinator. This is, of course, a minimum amount of time, and if a greater amount of time in the chlorinator is required, then the chlorinator must be larger in proportion to the travel rate of the cloth. With a pH held at essentially the neutral point 3 seconds appears to be about the minimum time in which to effect reaction of the chlorine with the sodium hydroxide in the cloth and to effect bleaching of the cloth by the hypochlorite produced by that reaction. As is well known, at a higher pH, a longer contact time will be required in order to effect reaction and bleaching.

While the size of the chlorinator determines the contact time of the cloth within the chlorinator saturator for a given rate of cloth speed, the rate of sodium hydroxide input with the cloth and the rate of chlorine input will determine the concentration of the hypochlorite bleach solution produced by the reaction. Generally, when operating at a pH of 6.6 to 7.4, there will be present in the solution about 0.1 to about 5 grams per liter of available chlorine. Under these conditions there will be no titratable alkalinity present in the aqueous solution. At concentrations higher than 5 grams per liter of available chlorine at essentially neutral pH, there is some damage to the cloth. Generally, a concentration of 0.5 to 2 grams per liter of available chlorine is preferred.

When alkaline conditions are preferred, that is, when the chlorinator is operated at a pH of 7.4 to 10.0, a much smaller range of available chlorine must be maintained in the solution. In this case the range of available chlorine will be 1 to 2 grams per liter. At higher concentrations the hypochlorite is carried into the peroxide saturator where it will decompose the peroxide unless J box retention time between the hypochlorite saturator and peroxide saturator is extended considerably beyond the usual 20 to 30 minutes. Alternatively, if the increased retention time is not provided, a water washing stage would have to be provided between the J box and peroxide saturator.

If additional bleaching by hypochlorite is desired over that which is provided by the chlorination of the sodium hydroxide retained by the cloth from the caustic scouring operation, additional bleach can be provided by either adding sodium hypochlorite solution to the chlorinator or by providing a separate introduction of sodium hydroxide together with increased amounts of chlorine.

Following the treatment in the chlorinator the cotton cloth passes through squeeze rollers and then moves directly into the hydrogen peroxide saturator without intermediate washing. The peroxide bleaching is accomplished by procedures which are well known in the art. Generally, the peroxide saturator is normally operated within a pH range of 10.4 to 10.8 and at a concentration of 3 to 15 grams of 100% peroxide per liter. The hydrogen peroxide is generally stabilized with sodium silicate in order to prevent excessive decomposition of the peroxide.

Our invention is also applicable to the cotton cloth finishing process which embodies a sodium hypochlorite bleaching stage and a hydrogen peroxide bleaching stage. In this case the hypochlorite bleaching stage would be prior to the peroxide bleaching stage. If residual alkalinity from the cloth is carried into the sodium hypochlorite bleaching stage, the pH of the hypochlorite will increase

and the rate of bleaching activity will decrease rapidly. Normally, sodium hypochlorite bleaching operations for cotton are conducted at a pH within the range of 7.4 to 10.0. If the pH goes above 10.0, then the time required for the bleaching is greatly increased. Because of the slow bleaching by the sodium hypochlorite of the color bodies in the cotton cloth at a pH of 10 or higher, a J box is required for the cloth to be stored in while it is undergoing bleaching with the hypochlorite. Retention time of the cloth in contact with the hypochlorite liquor varies from 20 to 60 minutes.

If there is residual alkalinity carried into the sodium hypochlorite, raising the pH above 10.0 and into the range of 11 or higher, the time allowed for reaction of the hypochlorite for the cloth in the J box will not be sufficient for complete reaction, and there will be a carry over of the hypochlorite into the peroxide saturator. The presence of the hypochlorite in the peroxide will cause a decomposition of the peroxide with its attendant loss. In this aspect of our discovery the pH of the alkaline hypochlorite saturator is controlled against an undesired increase in pH due to retained caustic in the cloth being processed by introducing chlorine gas preferably into the alkaline hypochlorite saturator. Here there will be a continuous introduction of alkali with the cloth into the chlorinator and continuous introduction of chlorine gas into the chlorinator with the rate of chlorine introduction being controlled by a pH controller.

There is another advantage to our process in that the introduction of chlorine gas into water in the presence of the cloth accomplishes a type of bleaching which cannot be obtained by sodium hypochlorite or peroxide. Thus, in our process of peroxide bleaching there is the bleaching action by the chlorine gas, the bleaching action by the hypochlorite produced from the retained alkalinity in the cloth and the bleaching action of the peroxide itself. Consequently, the cloth whiteness by our method of processing is far superior to the conventional processes. Alternatively, this increased bleaching can be used to effect savings in peroxide by bleaching to the whiteness normally produced by the peroxide alone. The process is set forth in flow sheet form in the accompanying drawing.

EXAMPLE 1

In a cloth processing train comprising a caustic soda steamer, a four compartment water washer, a two compartment water washer, a hydrogen peroxide saturator, a hydrogen peroxide steamer and a two compartment water washer, 1.72 yards per pound cotton twill was introduced to the process at a rate of 90 yards per minute or 5400 yards per hour. Following the caustic soda steamer, the water washing tanks were maintained with hot water at a temperature between 180° F. and approaching 212° F. The wet cloth leaving the fourth water washing tank had a pH of approximately 11 indicating large amounts of residual caustic soda.

Chlorine gas was introduced into the bottom of the first compartment of the two compartment washer which followed the four compartment washer. This compartment was filled with 400 gallons of water and maintained at a temperature of about 60 to 80° F. The warm cloth from the previous water washing stage maintained at a temperature of about 200° F. warmed the water to about 110° F. A chlorine diffuser was connected by piping through a rotameter and control valve to a chlorine cylinder.

As the cotton cloth progressed through the chlorinator, the chlorine flow was adjusted to produce a substantially neutral solution in the water in the compartment. Analysis of the solution indicated an appreciable available chlorine content but no titratable alkalinity. When the chlorine addition was interrupted, the available chlorine content of the solution quickly vanished and titratable alkalinity appeared, the pH of the solution rising to 10.7.

During the addition of chlorine no fumes or odors of chlorine were detected from the solution being chlorinated indicating good stability for the chlorine containing solution at the neutral pH point. About 5400 yards or 3000 pounds of cotton goods was processed in 1 hour during which time 6 pounds of chlorine was introduced. The cloth leaving the chlorinator was lighter in color and cleaner in appearance than the cloth entering the chlorinator. The following table shows the temperature conditions, the chlorine feed rate and the presence of available chlorine or titratable alkalinity in the chlorinator together with pH for various time intervals. Six pounds of chlorine was added during the 1 hour period.

Table 1

Time	Cl_2 Rotameter Reading (Uncorrected)	Temp. of Aqueous Solution, ° F.	g./l. Av. Cl_2	g./l. NaOH	pH	Cloth Whiteness [1]	Tensile Strength Scott Tester (average of ten breaks)	
							Warp	Filling
2:10 start	7 lb/hr. Increased							
2:20	13 lb./hr. Decreased		.13	.24				
2:30	9 lb./hr	110	.3	0	6.4	1.8	133	55
2:45	8 lb./hr	110	.42	0	6.8	2.1	144	56
2:55	6 lb./hr	110	.3	0	6.8			
3:10	6 lb./hr	110	.3	0	8.5			
3:12	Cl_2 off							
3:25	Cl_2 off	110	.04	.4	10.7	2.8	136	50

[1] Tristimulous measurements on Hunter reflectometer using green, blue and amber filters. Lowest positive numeral value is most white while a highest positive numerical value is most yellow.

EXAMPLE 2

The conditions of Example 1 were repeated with corduroy fabric and with chlorine introduced at the bottom of both compartments of the two compartment washer. At 10:05, without chlorination of residual alkali, the hydrogen peroxide feed pump was introducing 35% peroxide to the peroxide saturator at a rate of 35 seconds per minute. At 3:00 o'clock, with chlorination of the residual cloth alkali controlled so that the liquor in the compartments being chlorinated was at a pH of 6.0 and 6.2 respectively, the peroxide feed was reduced to a rate of 25 seconds per minute while still maintaining the equivalent bleach of the cloth at the higher rate of peroxide feed.

EXAMPLE 3

To prove the feasibility of providing additional chlorine bleaching to that provided by the residual alkalinity in the cloth sodium hydroxide was continuously introduced to a chlorinating vessel at a concentration of 4 grams per liter NaOH and continuously neutralized by the addition of chlorine gas. The chlorine rate in grams of chlorine per minute, the grams per liter of available chlorine in the aqueous solution and in the pH readings versus time are given in the table below. The initial solution was provided by the addition of 1140 ml. of concentrated sodium hypochlorite.

Table 2

CONTINUOUS PRODUCTION OF SODIUM HYPOCHLORITE FROM NaOH AND Cl_2

Time, Hrs-Mins.	g./l. Av. Cl_2	pH	g. Cl_2/min.
0—0	2.42		
0—10	2.42	9.3	.19
0—15	2.45	9.2	.19
0—25	2.94	7.3	.48
0—30			
0—40	4.15	6.8	.48
0—50	4.60	6.7	.48
0—55			.29
1—5	3.74	7.3	.29
1—15	3.30	7.9	.29
1—20			.38
1—30	3.46	7.6	.38
1—40	4.06	7.2	.38
1—45			.29
1—55	3.90	7.4	.29
2—5	3.86	7.4	.29
2—15	3.64	7.6	.29
2—20			.38
2—30	3.98	7.4	.38
2—40	4.60	7.2	.38
2—50	4.60	7.0	.38
3—0			
3—10	4.45	6.6	.38
3—15			.19
3—30	4.00	6.5	.19
3—35			.14
3—50	3.14	7.1	.14
4—5	2.50	7.6	.14
4—15			
4—20	2.04	8.1	.14
4—25			.29
4—35	1.88	7.6	.38
4—50	2.38	6.9	.38
5—5	2.14	6.2	.38
5—10			.29
5—20	2.44	6.5	.29
5—25			.19
5—40	2.02	6.8	.19

Samples of unbleached cloth were considerably bleached by immersion for about 30 seconds in the bleach removed at intervals throughout the production of the chlorine bleach liquor.

EXAMPLE 4

In a bleaching operation using neutral hypochlorite bleaching followed by peroxide bleaching, the pH was maintained by the addition of phosphoric acid. The cloth was introduced at a rate of 3000 lbs./hour at a speed of 90 yards per minute. The cloth leaving the water washing tanks following the sodium hydroxide treatment carried about 0.3% by weight sodium hydroxide into the sodium hypochlorite saturator. The saturator was fed continuously with 20 grams per liter of available chlorine sodium hypochlorite solution. The sodium hypochlorite solution and 75% phosphoric acid liquid was fed to the 400 gallon saturator by proportioning pumps. A continuous recording pH meter was placed in the chlorinator. The test run was started at 7 a.m. with 0.7 gram per liter available chlorine solution in the hypochlorite saturator at a pH of 6.6. The hypochlorite feed was adjusted to maintain this concentration of hypochlorite and the phosphoric acid was kept at a maximum rate of 1 gallon per hour. The cloth rate was 3000 pounds per hour and the chlorination machine held 400 gallons of solution. The temperature was held between 75 and 85° F. At 8:30 a.m. the pH of the solution began to rise and about 9:30 it was about 7.6, necessitating the addition of increased amounts of phosphoric acid to bring the pH down to 6.6 again. Additional water washing was provided for the cloth prior to its entry into the hypochlorite saturator, but this did not alleviate the increase in pH. The final bleaching results were satisfactory, but the cost of the added phosphoric acid more than offset any savings in the peroxide bleaching materials.

EXAMPLE 5

The conditions of Example 3 were repeated without any phosphoric acid addition. Within a period of 2½ hours, the pH of the hypochlorite saturator had increased from 7.0 to 11.2 due to the residual alkalinity in the cloth necessitating a shut-down of the processing.

EXAMPLE 6

Cotton cloth of a rope bleaching type was introduced at a rate of 300 yards per minute or 4000 pounds per hour to a hypochlorite saturator holding 200 gallons of sodium hypochlorite solution of 2.5 grams per liter of available chlorine at a pH of 10.8. Following this the cloth was introduced to a palstic J box which had a 15 minute cloth capacity. The hypochlorite saturator was fed from 20 grams per liter of available chlorine sodium hypochlorite stock solution. For a period of 2½ hours the cloth was bleached quite satisfactorily. Then the solution and the peroxide saturator began to take on a greenish, yellow tinge, and the whiteness of the cloth began to decrease. After 3½ hours, the cloth from the bleaching operation began to show signs of tearing so the operation was discontinued. The pH of the hypochlorite saturator at this time was 11.2, and the alkalinity of the peroxide solution had gone to the point where the operator had to stop feeding silicate thereby decreasing the stability of the peroxide solution.

We claim:

1. The process of continuously neutralizing residual alkalinity in cotton cloth derived from a caustic stage of a hydrogen peroxide bleaching process comprising introducing the cloth into an aqueous solution maintained at a pH within the range of 6.6 to 10 and with an available chlorine concentration of 0.1 to 5 grams per liter by the introduction of chlorine while maintaining the said solution at a temperature within the range of 60 to 120° F., retaining the cloth within the said solution for a period of at least 3 seconds and thereafter introducing the cloth into aqueous hydrogen peroxide.

2. The process of continuously neutralizing residual alkalinity in cottom cloth derived from a caustic stage of a hydrogen peroxide bleaching process comprising introducing the said cloth into an aqueous solution maintained at a pH within the range of 6.6 to 7.4 and with an available chlorine concentration of 0.1 to 5 grams per liter by the introduction of chlorine while maintaining the said solution at a temperature within the range of 60 to 120° F., retaining the cloth within the said solution for a period of at least 3 seconds and thereafter directly introducing the cloth into aqueous hydrogen peroxide.

3. The process of continuously neutralizing residual alkalinity in cottom cloth derived from a caustic stage of a hydrogen peroxide bleaching process comprising introducing the said cloth into an aqueous solution maintained at a pH within the range of 7.4 to 10.0 and with an available chlorine concentration of 1 to 2 grams per liter by the introduction of chlorine and thereafter holding the cloth in a J box for a time sufficient for available chlorine bleaching to take place and thereafter introducing the cloth into aqueous hydrogen peroxide.

4. In a process for bleaching cotton cloth which includes successive caustic scouring stage, sodium hypochlorite bleaching stage and hydrogen peroxide bleaching stage, the method of preventing the residual alkali on the cloth from increasing the pH in the hypochlorite bleaching stage comprising introducing a regulated amount of chlorine to the said hypochlorite stage to maintain a pH within the range of 6.6 to 10 and an available chlorine concentration of 0.1 to 5 grams per liter.

References Cited in the file of this patent

UNITED STATES PATENTS

1,568,664	Geisler	Jan. 5, 1926
1,908,481	Kauffmann	May 9, 1933
2,048,991	Butz et al.	July 28, 1936
2,165,270	Kauffmann	July 11, 1939
2,960,383	Potter et al.	Nov. 15, 1960

OTHER REFERENCES

Melliand: Textiberichte, vol. 24, 1943, pp. 24–26.

Soap and Sanitary Chemicals, September 1944, 20: 9, pp. 115 and 117.