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AQUEOUS BLEACHING SOLUTION

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The present discovery relates to improvements in the bleaching of certain colored yarn fabrics. More particularly, this discovery relates to improved bleaching processes and compositions for the prevention of staining and mark-off of naphthol dyed colored yarn fabrics.

Colored yarn fabrics are those in which previously dyed yarns are used, usually in conjunction with undyed yarns, in the weaving. By naphthol dyes is meant those dye stuffs which contain within their molecular structure a hydroxynaphthalene group. Because of the desirable color effects which they produce, such dyes are used on a large portion of all colored yarn. Fabrics woven from naphthol dyed yarn have for years posed a problem in textile bleaching operations because of their tendency to stain and "mark-off" on their own undyed portions and on other goods. Most other yarn dyed fabrics are colored with vat dyes and these fabrics are readily peroxide bleached without serious stain or mark-off problems. Because the naphthol dyed and the vat dyed colored yarn fabrics are sewn together and inter-mixed in bales of gray goods coming from the weaving mill, substantial labor is involved in separating the more sensitive naphthol dyed fabrics for special treatment.

Since the owners of the fabrics require that they be delivered together in the same batch as they were delivered to the bleachery, the vat yarn dyed fabrics must be stored until the naphthol dyed fabrics have been bleached. Such storage frequently amounts to more than a week and involves a serious handling problem in addition to requiring the bleachery to operate with larger warehouse storage areas.

The present discovery offers a new process and new compositions for the bleaching of both vat dyed and naphthol dyed goods in a single operation without the necessity of segregating them by types of dye and without the requirement of any additional treatment steps over those now used for the less sensitive vat dyed goods.

It is well known that a hydrogen peroxide solution which contains silicate of soda together with soda ash or bicarbonate of soda and which has a pH of 10 and a temperature of not over 150° F. can be used to bleach naphthol dyed yarn fabrics with little or no strain or mark-off. Such operations are performed in kiers using a water ratio of 5:1 or higher, i.e. 5 parts by weight of solution to 1 part of cloth; and the bleaching cycle requires about 8 hours.

A few of the larger bleacheries have discovered that they can continuously steam bleach naphthol dyed yarn fabrics after scouring with a hydrogen peroxide, silicate of soda and bicarbonate of soda solution at a pH of about 10. The bleaching solution is applied in a saturator which must be maintained at a constant level for successful continuous operation. The fabric comes into the saturator in a wet condition (approximately 1 part of water to 1 part of cloth) and leaves the saturator with the same degree of wetness. Thus, for each pound of cloth entering, a pound of water is deposited in the saturator, and a pound of bleaching solution is removed. In order to maintain the strength of the bleaching solution in the saturator, a feed tank containing hydrogen peroxide, silicate of soda and bicarbonate of soda in a concentration of at least 7 times that desired in the saturator must be used to continuously supply the chemicals taken out by the fabric.

A feed tank solution which contains hydrogen peroxide, sodium silicate and bicarbonate soda in sufficient concentrations to maintain a bleaching solution of suitable strength with a pH of not over 10.0 in the saturator will rapidly form a gel and become useless. This tendency to gel cannot be overcome by any practical degree of agitation nor by heating the solution to any reasonable temperature.

A further serious problem is posed in continuous bleaching of these naphthol dyed colored yarn fabrics because the silicate of soda-bicarbonate of soda-peroxide solution has a strong tendency to crystallize out on hot surfaces. After leaving the peroxide saturator, the cloth is generally fed to a J-box where the steam bleaching process takes place. In passing through the J-box the cloth slides under pressure against the smooth surfaces of the box. Bleaching solutions of the sodium silicate-bicarbonate of soda type have a tendency to solidify on the hot walls of the J-boxes forming hard rough deposits which abrade cloth sliding against them, and which are often removed only by stopping production and completely emptying the J-box of fabric.

The present invention involves the use of certain new bleaching compositions and processes which permit the bleaching of both naphthol and vat dyed colored yarn fabrics together in the same batch, and which eliminate gelling in the chemical feed tank, and crystallization of bleach solutions on the surface of the J-box. All of these valuable improvements are accomplished by the complete elimination of the sodium silicate which has been traditionally used in bleaching solutions and its replacement with a carefully determined quantity of an alkali metal carbonate balanced by a proper amount of an alkali metal bicarbonate.

In bleaching fabrics containing naphthol dyed yarns, three factors are most important to the prevention of staining and mark-off. These are: peroxide concentration (which should be as low as possible), pH (which should be maintained in all cases at or preferably below 10.0) and total alkalinity as measured by the use of phenol red indicator (which should be as high as possible).

The present invention offers new methods for preparing bleaching solutions which meet the three above mentioned criteria, and which have little or no tendency to gel or precipitate out in J-boxes. Thus there has been discovered a new process for the bleaching of naphthol dyed colored yarns which permits brightening of excellent quality with so little staining and mark-off that vat dyed colored yarn fabrics may be bleached simultaneously with naphthol dyed.

By total alkalinity is meant the amount of alkali present as measured by titrating a measured quantity of the solution with a standardized dilute acid solution until a phenol red end point is reached. The result may be expressed in terms of the grams per liter of NaOH which that amount of acid would neutralize, or alternatively in terms of normality, that is, the number of moles of alkali per liter multiplied by the number of OH^- groups in the molecule.

In kier bleaching, solutions composed of hydrogen peroxide either with silicate of soda and soda ash, or, alternatively, with silicate of soda and bicarbonate of soda can be used to satisfactorily bleach naphthol dye colored yarn fabrics at a solution to cloth ratio of six to one. However, in continuous bleaching, which involves a solution to cloth ratio of about 1:1, the bleaching solution in the saturator must be several times as concentrated as that used in kier bleaching. Further, as discussed previously, because of the water brought into the saturator by the previously wetted cloth, the saturator solution must be continuously replenished from a head tank having a concentration of about seven times that of the chemicals in the saturator.

The more dilute solutions used in the kier bleaching processes pose few problems, but the concentrated solutions required in the head tanks in continuous bleaching processes exhibit a strong tendency to gel due to the sodium silicate which they contain. This gelling problem is intensified by hardness in the water used for dilution but exists even when de-ionized water is used. Chemical feed tanks are clogged; pipes are stopped; and precipitation and crystallization on J-box surfaces becomes severe.

In contrast, by eliminating the sodium silicate and incorporating from about 2.0 to about 30 grams/liter of an alkali metal bicarbonate together with a sufficient quantity of an alkali metal carbonate to cause the resulting bleaching solution to have a pH of from 9.5 to about 9.9, the present invention achieves an alkalinity of from about 0.05 to 1.0 normal. This alkalinity is higher than can be produced in any conventional bleaching solution having a pH below the critical level of 10 and contributes materially to bleaching efficiency. Further, these new solutions have little or no tendency to gel.

The substantial increase in the total alkalinity available in a solution below the critical pH level permits more efficient bleaching of the naphthol dyed colored yarn fabrics while still maintaining superior levels of bleaching quality. As an additional advantage, this bleaching can be achieved at relatively low temperatures and in certain instances can be obtained by a cold bleaching process performed entirely at room temperature.

In order to illustrate the problems solved by the present invention, a series of silicate-containing bleaching solutions having low pH was made up as shown in Table I.

TABLE I

Water, cc.	Sodium Silicate, g.	Hydrogen Peroxide, g.	Sodium Bicarbonate, g.	pH	Total Alkalinity	Observed
1,000	48.0	7.2	0.0	10.6	.026 N	No gel.
1,000	48.0	7.2	12.0	9.9	.048 N	No gel.
1,000	48.0	7.2	14.0	9.8	.050 N	Cloudy.
1,000	48.0	7.2	15.0	9.8	.050 N	Gel.
1,000	48.0	7.2	17.0	9.7	.052 N	Gel.

It will be noted from the above table that increasing the sodium bicarbonate content above 14 grams per liter causes gelling of the solution, and that even with a concentration of 17 grams per liter of sodium bicarbonate the total alkalinity is only 0.52 normal. This level of alkalinity is lower than is desirable for most efficient bleaching, since more hydrogen peroxide will be required than if the total alkalinity were in the area of 0.080 normal. Use of additional quantities of hydrogen peroxide is uneconomical and may affect colors causing them to change shade or become flat or dull.

While the present invention offers its greatest advantage in a continuous bleaching process conducted in saturators and J-boxes of the usual sort, certain specialized applications of the invention may involve its use in kiers or in dyeing equipment, or even in laundry washers. In all continuous operations, cloth-to-bleaching solution ratios of about 1:1 or less are desirable in the goods leaving the saturator. In batch operations, cloth-to-bleaching solution ratios of about 4:1 or above are preferred.

Bleaching times will vary widely according to the goods to be bleached, the equipment used, the nature of the process, and the concentration of the bleaching solution. In general, in single stage continuous bleaching, bleaching time will be from about one-half hour to one hour; in two-stage continuous operations, bleaching time will total about one to two hours. In batch operations in jigs and other dyeing machines, bleaching time will generally be between one and four hours. In kiers bleaching time will be from four to about eight hours.

The preferred temperature range for continuous bleaching is from about 150° to about 160° F. This temperature is required in continuous J-box operations in order to bleach satisfactorily while maintaining the minimum cloth throughputs required by the equipment. The preferred range for batch type bleaching machinery will also be between 150 to about 160° F. in order that the equipment time will be held to a reasonable minimum. In cold bleaching operations where goods are saturated in relatively concentrated bleaching solutions at ratios of about 1:1, then batched (i.e. roped, folded in the open width, or rolled into a suitable storage place where the material is prevented from drying out for about eight hours or until bleaching is complete) and then washed and dried conventionally; the saturator bleaching solution may be at room temperature.

In preparing the solutions for a typical continuous bleaching operation, a mixing tank with a propeller type agitator will generally be employed. The water will be at room temperature or, if convenient, may be heated. Generally the sparingly soluble stabilizer will be added first, followed by the bicarbonate of soda, carbonate of soda, wetting agent, in any order, and lastly the hydrogen peroxide. After the head tank has been filled, the saturator is loaded to about six-sevenths of its operating volume with water and the remaining seventh is filled with the concentrated head tank solution.

The method of preparation of the solution is not critical and a number of variations may be adopted to suit various circumstances. It may sometimes be more convenient to mix the bicarbonate of soda and carbonate of soda with water in one tank, and add the remaining water to hydrogen peroxide stabilizer and wetting agent in a second tank. The solutions from these two tanks may then be drawn directly into the saturator and the relative proportions of the solutions in the two tanks may be varied in order to increase or decrease the ratio of hydrogen peroxide to the alkalis.

For maximum economy and bleaching efficiency it is generally desirable to add about .05 to 1.0 gram per liter of bleaching solution stabilizer, preferably that disclosed in U.S. 2,838,459 to Sprout. This stabilizer may be added either to the bleaching solution or, in a concentration of about 0.35 to 7.0 grams per liter, to the head tank solution.

The present invention will work satisfactorily with any of the conventional desizing or combination desizing and mercerizing processes which are commonly employed by the industry.

Persons skilled in the bleaching art may also find it expedient to treat certain fabrics in certain continuous bleaching equipment by first desizing the fabrics as necessary, then wetting them in a saturator with a relatively dilute bleaching solution (generally representing the head tank solutions discussed above diluted in a ratio of one part of head tank solution to ten or more parts of water), then bleaching in a steam heated J-box for about one-half hour, then removing the textiles from the first J-box, resaturating them with a second bleaching solution (similar to the first) and treating them in a second J-box for approximately an additional one-half hour. This technique is particularly useful where the equipment available requires a relatively high throughput of cloth in terms of yards per minute.

The following examples will serve to illustrate the practice of the present invention but should not, of course, be considered as limiting it in any respect.

Example 1

Approximately 300 yards of cotton goods having one inch blue and green stripes of vat dyed colored yarn alternating with white background is sewn to a length of approximately 300 yards of naphthol dyed red and white striped cotton cloth. The dry cloth is first desized and then is fed to a bleaching saturator containing a solution of 100 gallons of water, 0.5 pound of stabilizer, 5 pounds

of sodium carbonate, 5 pounds of sodium bicarbonate, 8 pounds of 35% hydrogen peroxide. This saturator is fed with a solution from a head tank containing

Water	gallons	100
Sodium carbonate	lbs	35
35% hydrogen peroxide	lbs	56
Sodium bicarbonate	lbs	35

This solution has a pH of about 9.9 and a total alkalinity of 0.25 normal. The squeeze rolls on the exit of the saturator are set to yield a cloth to bleaching solution ratio of 1:1. The cloth is run through a steam heated J-box so that each portion of the cloth receives an exposure of one hour to the 150° to 160° F. temperature in the interior of the J-box. The cloth is fed to washers and all bleaching solution is removed. After drying, both the naphthol dyed and the vat dyed colored yarn fabrics which have been treated identically throughout the bleaching processs, show excellent whiteness and excellent brightness of color without evidence of running, staining, or mark-off.

Example 2

Approximately 300 yards of cotton goods having one inch blue and green stripes of vat dyed colored yarn alternating with white background is sewn to a length of approximately 300 yards of naphthol dyed red and white striped cotton cloth. The cloth is first desized and then fed to a bleaching saturator containing a solution composed of:

	Parts (by weight)
Water	1000
Sodium silicate	12
Sodium carbonate	1.2
Sodium bicarbonate	0
35% H_2O_2	9.6

The saturator is fed from a head tank containing a solution composed of:

	Parts
Water	1000
Sodium silicate	84
Sodium carbonate	8.4
Sodium bicarbonate	0
35% H_2O_2	67.2

The solution in the saturator has a total alkalinity of 0.06 normal, a pH of 10.5 and is at room temperature. The cloth is run into a steam heated J-box slowly and is slowly withdrawn so that each portion of the cloth receives an exposure of about 1 hour to the 150° temperature in the interior of the J-box. The bleached cloth is fed to washers and all bleaching solution residue is removed. After drying, the cloth is examined. Bleaching quality of vat dyed goods is satisfactory but the naphthol dyed goods show, particularly in the white areas, a large amount of staining and mark-off. The naphthol dyed goods are not suitable for sale.

Example 3

Using similar goods and identical equipment, the procedure of Example 2 is repeated with the following bleaching solutions and conditions.

Head tank solution composition:	Parts
Water	1000
Sodium silicate	48
Sodium carbonate	0
Sodium bicarbonate	12
35% H_2O_2	48
Saturator solution composition:	
Water	1000
Sodium silicate	9.6
Sodium carbonate	0
Sodium bicarbonate	2.4
35% H_2O_2	9.6

The total alkalinity of the bleaching solution in the saturator is 0.04 normal and the pH is 10.0, and the solution is at room temperature.

After passing through the J-box, washer and drier as in Example 2, the cloth is examined. The naphthol dyed goods show no mark-off and less staining, but are still not suitable for sale. The vat dyed goods continue to show satisfactory bleaching.

The head tank solution in this example is limited to five times the concentration desired in the saturator because when a more desirable concentration of seven times that desired in the saturator is prepared in the head tank, severe gelling and clogging of pipes and precipitation on J-boxes is experienced.

Example 4

Again using similar quantities and types of fabrics, identical equipment and similar desizing, steaming, washing and drying operations, the process of Examples 2 and 3 is repeated according to the method of the present invention, using the following bleaching compositions.

Head tank:	Parts
Water	1000
Sodium silicate	0
Sodium carbonate	84
Sodium bicarbonate	84
35% H_2O_2	67.2
Saturator:	
Water	1000
Bleaching solution stabilizer	0.5
Sodium silicate	0
Sodium carbonate	12
Sodium bicarbonate	12
35% H_2O_2	9.6

Here the total alkalinity in the saturator rises to 0.16 normal, a very desirable characteristic for the bleaching solution. The pH is 9.8 and the saturator remains at room temperature. After steaming, washing and drying as before, the goods are examined. The vat dyed fabrics again show good to excellent bleaching, and in addition the naphthol dyed goods show excellent bleach with no staining and no mark-off.

It should be noted that the head tank concentration in this example represents approximately 7 times the concentration used in the saturator. This desirable concentration ratio is obtained with no clogging of pipes or precipitation in J-boxes due to gelling of the solutions.

Example 5

Vat and naphthol dyed goods similar to those used in the preceding examples are bleached in a small kier, using a solution composed of:

	Parts
Water	1000
Sodium silicate	6
Sodium carbonate	1.2
Sodium bicarbonate	0
35% H_2O_2	4

The kier is brought by indirect steam heat to a temperature of about 160° F. and held at that temperature for about 7 hours. The bleaching solution has a total alkalinity of 0.04 normal and a pH of 10.2.

The goods are then washed and dried conventionally. The bleaching solution in the kier appears colored and on examination, the vat dyed cloth has a fair to good bleach but the naphthol dyed cloth shows both staining and some mark-off and is not suitable for sale.

Example 6

Using the same kier as in Example 5, similar cloth is bleached with the following solution:

	Parts
Water	1000
Sodium silicate	9.6
Sodium carbonate	0
Sodium bicarbonate	2.4
35% H_2O_2	4

This solution has a total alkalinity of 0.04 normal, a pH of about 10.0 and a temperature of 160° F. is maintained for about 7 hours in the kier.

After the bleaching cycle, the kier solution is found to be clear. The cloth after washing and drying shows mark-off and no stain on either the vat dyed or naphthol dyed, but the bleach is of only fair quality, probably due to the lower pH accompanied by the low total alkalinity.

Example 7

Using the same kier as in Examples 5 and 6, similar naphthol and vat dyed goods are bleached according to the method of the present invention, using a solution having the following composition:

	Parts
Water	1000
Bleaching solution stabilizer	0.5
Sodium silicate	0
Sodium carbonate	12
Sodium bicarbonate	12
35% H_2O_2	4

This bleaching solution has a total alkalinity of 0.12 normal, marked increase over that of the solutions in the two preceding examples, and the pH is now lowered to 9.8, the temperature is 160° F. and the bleaching time is as in the two preceding examples.

After the cloth is removed, the kier solution is still clearer than in Example 6 and both vat and naphthol dyed fabrics are free from mark-off and stain and show good to excellent bleach.

Example 8

A bleaching solution consisting of the following ingredients is prepared and transferred to a saturator:

	Parts
Water	1000
Sodium silicate	36
Sodium carbonate	0
Sodium bicarbonate	0
35% H_2O_2	30

With the solution at 70° F., a length of about 300 yards of naphthol dyed striped goods and about 300 yards of vat dyed striped goods identical to those in the preceding examples are introduced. This solution has a total alkalinity of about 0.12 normal and a pH of about 11.0. The temperature remains at all times at about 70° F. The goods are batched for about eight hours and are then washed and dried.

Examination of the cloth after washing and drying shows good bleaching quality but some staining and some mark-off.

Example 9

Using the techniques and goods identical with those used in Example 8, bleaching is carried out using the following solution:

	Parts
Water	1000
Sodium silicate	21.6
Sodium carbonate	0
Sodium bicarbonate	4.8
35% H_2O_2	30

This solution has a total alkalinity of 0.08 normal, a pH of 10.4 and is maintained at about 70° F. throughout the bleaching period of approximately eight hours.

Examination of the cloth after conventional washing and drying indicates no mark-off and less stain than in the preceding example, but the bleaching is only fair and the staining that occurs is sufficient to prevent the goods from being marketable.

Example 10

Using the same techniques as in the two preceding examples, cloth identical to that bleached in the preceding examples is bleached according to the present invention

by batching for eight hours after being saturated with a 70° F. solution having the following composition:

	Parts
Water	1000
Bleaching solution stabilizer	0.5
Sodium silicate	0
Sodium carbonate	20
Sodium bicarbonate	20
35% H_2O_2	30

This solution has a total alkalinity of 0.25 normal, a pH of 9.9 and the 70° F. temperature is maintained throughout the batching period.

Examination of this cloth after conventional washing and drying shows no mark-off of either the naphthol or vat dyed fabric, no staining of either fabric and goods to excellent whiteness and brightness of colors in both fabrics.

The composition of the aqueous bleaching solutions which contact the cloth in the practice of the present invention will fall within the ranges given below:

2.0 to 50 grams/liter of 100% hydrogen peroxide,
2.0 to 50 grams/liter of alkali metal bicarbonate,
and a sufficient quantity of alkali metal carbonate to cause the solution to have a pH between 9.5 and 9.9 and an alkalinity from 0.05 to 1.0 normal.

As mentioned before, stabilizers may be added where desired, and other special purpose ingredients may be found advantageous in certain instances, but none of these is essential to the practice of the invention.

Within the above broad compositions, more narrow ranges will be preferred for certain specialized bleaching processes, as illustrated by the preceding examples numbered 1, 4, 7 and 10.

For continuous bleaching the ranges of composition which are especially preferred are:

2.0 to 4.0 grams/liter of 100% hydrogen peroxide,
5 to 15 grams/liter of alkali metal bicarbonate,
and a sufficient quantity of alkali metal carbonate to cause the solution to have a pH between 9.5 and 9.9 and an alkalinity from 0.05 to 1.0 normal.

For kier bleaching processes the preferred bleaching solutions will comprise:

2.0 to 4.0 grams/liter of 100% hydrogen peroxide,
2.0 to 20 grams/liter of alkali metal bicarbonate,
and sufficient alkali metal carbonate to cause the solution to have a pH of between 9.5 and 9.9 and an alkalinity of from 0.05 to 0.20 normal.

The preferred solution for cold bleaching will comprise:

2 to 30 grams/liter of 100% hydrogen peroxide,
10 to 25 grams/liter of sodium bicarbonate,
and sufficient alkali metal carbonate to cause the solution to have a pH between 9.5 and 9.9 and an alkalinity from 0.05 to 1.0 normal.

Especially preferred cold bleaching solutions are those in the above-mentioned range which contain from 10 to about 25 grams/liter of sodium carbonate.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the scope and spirit thereof, and the invention includes all such modifications.

What is claimed is:

An aqueous bleaching solution for textile and garment materials, portions of which are naphthol dyed having a pH between 9.5 and 9.9 at an alkalinity within the range of from 0.05 to 1.0 normal, said aqueous solution consisting essentially of

10 to 25 grams per liter of sodium carbonate,
10 to 25 grams per liter of sodium bicarbonate, and
2 to 30 grams per liter of hydrogen peroxide.

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