United States Patent Office

3,043,645

Patented July 10, 1962

3,043,645

IMPROVED METHOD OF DYEING CELLULOSIC FIBERS WITH INDOCARBON BLACK SULFUR DYESTUFF

Glenn F. Womble, Danville, Va., assignor, by mesne assignments, to Martin-Marietta Corporation, Chicago, Ill., a corporation of Maryland

No Drawing. Filed July 22, 1959, Ser. No. 828,689
3 Claims. (Cl. 8—37)

This invention relates to improved processes of dyeing fibers, particularly cotton fibers, and the like with sulfur colors, particularly Indocarbon black, and dyed fibers obtained thereby.

Haller in United States Patent Number 1,874,099, dated August 30, 1932, describes a method of dyeing cotton with sulfurized carbazole-p-nitrosophenol dyestuffs by impregnating fibers with the dye and thereafter treating them with a diazo compound in the presence of sodium acetate while the dye is still in its leuco form. This method has the disadvantage of seriously damaging the tensile strength of the dyed fibers.

In another United States Patent Number 1,879,727, Bommer, Haller, and Pool described a method of dyeing fibers of all kinds with certain vat dyestuffs including the products of sulfurization of carbazole-p-nitrosophenol by first making a dyeing and thereafter treating the substantially fully developed dyed fibers with a diazo compound in the presence of an excess of sodium acetate. The Bommer et al. method has the disadvantage of failing to produce good properties of fastness to chlorine, peroxide and the like.

The process of this invention is particularly advantageous in yarn dyeing machines wherein fluid, i.e., the dye liquor, wash liquor, etc., is circulated through yarn packages or beams. The yarns dyed in such machines are ordinarily woven with white or colored yarn into various designs such as striped, checkered, and plaid fabrics which are chlorine- and/or peroxide-bleached. Thus, the dyed yarns must possess substantial resistance to bleaching. Sulfur color dyeings are notoriously unstable to the action of bleaching agents and heretofore have been employed only in those areas of use wherein there is no necessity or desire for bleaching. Almost all commercial machine dyeing of cotton yarn for obtaining optimum fastness properties has heretofore been done with expensive anthraquinone vat colors, especially when dyeing blacks.

One object of this invention is to obviate the disadvantages encountered in the prior methods of treating sulfur color dyed fibers with diazo compounds.

Another object of the invention is to provide a process of dyeing yarns with Indocarbon black sulfur colors to obtain fastness properties equal or in some cases superior to those obtained with good anthraquinone vat colors.

Another object is to provide yarns and a process of dyeing yarns which when made into checks, plaids, and the like with white yarn and then bleached, for example, with hydrogen peroxide, do not bleed objectionably into the white areas.

Another object of the invention is the production of yarn-dyed woven patterns such as checkered, plaid, and similar fabrics at a greatly reduced color cost.

Other objects are to provide yarns and a process of dyeing yarns with sulfur colors to obtain improved fastness properties without substantial sacrifice in tensile strength.

Other objects of the invention will be more readily apparent from the following detailed description of the invention.

Broadly, the process of this invention, described in

reference to Indocarbon black dyes, includes oxidizing the leuco form of an Indocarbon black sulfur color as applied to fibers, to an intermediate but still reactive stage, with air and treating the so-oxidized dyeing with a diazo compound under substantially non-oxidizing conditions. I have found that when the leuco Indocarbon black sulfur color dyed fibers are treated with a diazo compound, the fibers are degraded as evidenced by a lower tensile strength. I have also found that Indocarbon black sulfur color dyeings, which have been oxidized in the usual manner, are in a substantially fully developed state of oxidation, i.e., beyond the intermediate stage and at which no substantial further rapid oxidation takes place under ordinary conditions of use. No improvement in bleach-fastness is obtained after treating such substantially fully developed, or oxidized, dyeings with a diazo compound.

Specifically, this invention is based on the remarkable discovery that air-oxidation of the leuco Indocarbon black as well as certain other sulfur colors, when applied to materials being dyed, to an intermediate stage provides much improved fastness to bleaching after reaction with a diazo compound. The dyed fibers furthermore undergo no significant loss of tensile strength.

Intermediate oxidation by air is carried out in any suitable manner which will leave a portion of the sulfur color in the not-completely-oxidized form.

After oxidation by air, it is important to prevent any substantial further oxidation of the Indocarbon black sulfur color. Although the exact theory or detailed reaction mechanism underlying the results obtained by my novel process has not been definitely established, it is believed that a range or degree of oxidation between the leuco and substantially fully developed state is necessary to achieve optimum results. Oxidation with air for periods ranging from about ten minutes up to twenty-four hours, for example, is unique in providing that level of oxidation which results in outstanding bleach-fastness without damaging the strength of the dyed fibers during treatment with the diazo compound. Any substantial oxidation beyond the level just described and toward the substantially fully developed state of oxidation by extended exposure to air or by treatment with chemical oxidants prior to or during treatment with the diazo compound decreases the degree of bleach-fastness in the resulting dyeings.

The usual practice in prior art dyeing with many sulfur colors in package and beam dyeing machines is to develop the color by the use of chemical oxidants as opposed to air. However, the chemical oxidants, e.g., sodium perborate, hydrogen peroxide, ammonium persulfate and the like, as ordinarily employed, oxidize the sulfur dyeings beyond the level required for successfully carrying out the present invention. Furthermore, when such chemical oxidants are employed in attempts to oxidize the sulfur dyeings to an intermediate stage, the oxidation is difficult, if not impossible, to control practically. However, air forced into the dyeing machine and through the yarn oxidizes the applied leuco sulfur dye to an intermediate stage and, thus, is unique.

After air oxidation to an intermediate stage just described, the Indocarbon black dyeing is then treated with a diazo compound prepared by methods conventionally employed in naphthol dyeing, but preferably without neutralization of the mineral acid used in the diazotization. However, any substantial additional oxidation should be avoided.

One possible source of oxidizing power during treatment with the diazo compound is any residual nitrous acid (or nitrite convertible to nitrous acid) remaining from the diazotization in preparing the diazo compound. Residual nitrous acid is advantageously removed by adding to the diazo solution an agent which will react with the nitrous acid and eliminate the nitrogen (or nitrite). Particularly useful materials for eliminating residual nitrous acid include sulfamic acid and urea. Sulfamic acid also stabilizes the solution of the diazo compound, presumably by providing a suitably low pH without the presence of nitrous acid.

Treatment of the intermediate stage, air oxidized, Indocarbon black dyeing with the diazo compound is accompanied by the evolution of a gas, evidencing a chemical reaction. Although the mechanics of such a reaction is not fully understood, the reaction has been found to be necessary in the attainment of bleach-fast dyeings. The usual sulfur dyeings, i.e., those which are normally prepared for end use, e.g., in a fabric, being in a fully developed state of oxidation, have not been observed to evolve a gas when treated with the diazo compound.

The Indocarbon black sulfur colors employed herein have the Prototype No. 126, and the New Color Index No. Sul. Blk. 11. They are available commercially as SoDyeCo Fast Liquid Black G, SoDyeCo Fast Liquid Black R, and Indocarbon CLGS [1] Liquid.

Preparation of the dyebath and Indocarbon black sulfur color leuco dyeings therefrom are carried out according to well-known methods or any other suitable method.

The diazo compounds, otherwise known as diazotized amines, are prepared in accordance with conventional procedures. In general, diazo compounds are usually prepared by the diazotization of bases with a nitrite, e.g., sodium nitrite, in an acidic medium. Typical of the bases which are diazotized and used as diazo compounds in my process are the aryl amines including Fast Scarlet GG Base (2,5-dichloroaniline), Fast Yellow GC Base (o-chloroaniline), Fast Orange GC (m-chloroaniline) and the like, or their corresponding color salts. Other bases such as listed below can be employed to provide improved bleach fastness without substantial reduction in tensile strength in accordance with the process described herein.

Manufacturer's Name	Chemical Name
Fast Scarlet G Base	p-nitro-o-toluidine.
Fast Scarlet R Base	5-nitro-2-anisidine.
Fast Scarlet TR Base	3-chloro-2-methylaniline.
Fast Scarlet LG Base	benzyl-1-methyoxy-2-aminophenyl-4-sulfone.
Fast Scarlet RC Base	p-nitro-o-anisidine.
Fast Red RC Base	p-chloro-o-anisidine.
Fast Red GG Base	p-nitro-aniline.
Fast Red GL Base	m-nitro-p-toluidine.
Fast Red 3GL Base	p-chloro-o-nitroaniline.
Fast Red RL Base	m-nitro-o-toluidine.
Fast Red B Base	p-nitro-o-anisidine.
Fast Red TR Base	5-chloro-2-aminotoluene.
Fast Red ITR Base	diethyl sulfonamido-o-anisidine.
Fast Red KB Base	p-chloro-o-toluidine.
Fast Red FG Base	4-chloro-2 aminodiphenyl oxide.
Fast Bordeaux GP Base	m-nitro-p-anisidine.
Fast Garnet GBC Base	o-aminoazotoluene.
Fast Blue B Base	dianisidine.
Fast Blue BB Base	5-amino-2-benzoylamino-1,4-diethoxy benzene.
	2,4-dichloroaniline.
Fast Black LB Base	o-anisidine azo-a-naphthylamine.
Fast Orange GR Base	o-nitroaniline.

While the process of this invention is generally applicable to the dyeing of any fibers, capable of being dyed with sulfur colors ordinarily used on cotton and the like, in woven or unwoven form, it is particularly adaptable to dyeing cellulosic fibers and especially, cotton fibers. Fibers dyed in accordance with the process of this invention can be treated with such agents as chlorine or hydrogen peroxide without any substantial loss of color.

My process is particularly useful in dyeing cotton yarns which are to be interwoven with white yarns or other colored yarns to form a fabric having a certain design. Cellulose textile fabrics, yarns, or knitted goods thus made and comprising interwoven white (or other colored yarns), especially cotton yarns, dyed by my process are characterized by the ability to be bleached without the dyed yarns running and/or staining appreciably the adjacent white yarns.

Improved bleach and wash fastness without substantial impairment of tensile strength is also obtained with other sulfur colors when employed in accordance with the process for dyeing with Indocarbon blacks as described herein. The following list illustrates the various sulfur colors which are advantageously employed in place of the Indocarbon black sulfur colors in the process as described herein.

Manufacturer's Name	Color Index or Prototype No.	Part I—New Color Index No.
Sulfogene [1] Brown C14R	Pr. 702	Sul. Red 5.
SoDyeSul [1] Liquid Yellow ECF	955	Sul. Yell. 4.
SoDyeSul [1] Liquid Brown FLCF	Pr. 702	Sul. Red 5.
SoDyeSul [1] Liquid Green BGCF		Sul. Green 16.
SoDyeSul [1] Liquid Green NJ		

[1] Trademark.

The following examples are presented.

In the examples, percentages unless otherwise specified are based on the weight of fiber being treated. Chlorine bleaching employed in the examples to determine chlorine-bleach fastness was conducted by treating about 1 gm. of the dyed fiber with 100 cc. of water containing 2 g./l. available chlorine at room temperature for a period of one hour. The available chlorine is provided by sodium hypochlorite.

Hydrogen-peroxide bleaching employed in the examples to determine peroxide-bleach fastness involved the following procedure. A portion of the dyed fiber wrapped with a swatch of white cotton cloth (prepared for dyeing) is steeped in a solution containing the following ingredients:

Anhydrous disodium phosphate	g./l.	10
Borax	g./l.	5
Calcium chloride	g./l.	0.2
28% aqueous hydrogen peroxide	cc./l.	12.5

This solution has a pH of about 10 and titrates 4.5 to 5 g./l. hydrogen peroxide. The fiber wrapped in the white cloth is then inserted into a tube, and the tube is stoppered with provision for exhaust vapors. The tube is then placed in a boiling water bath as a means of heating, for one hour. The hydrogen-peroxide bleaching described above is essentially the same as bleaching conducted in textile plants.

Bleach-treated fibers, whether treated by chlorine or hydrogen peroxide, were then visually compared with unbleached, dyed fibers to determine the degree of color loss. No substantial degree of color loss designates excellent bleach fastness, noticeable but minor color loss designates good bleach fastness, substantial color loss designates fair bleach fastness and almost total color loss designates poor bleach fastness. Also, as an indication of bleach fastness, the white cotton swatches wrapping the dyed fibers and subjected to the hydrogen-peroxide bleaching were inspected. Substantially no coloring of the white cloth designates excellent bleach fastness, barely noticeable discoloration of the white cloth designates good bleach fastness, substantial coloring of the white cloth designates fair bleach fastness and substantially heavy coloring of the white cloth designates poor bleach fastness.

The bases with the exception of Fast Scarlet GG were diazotized in the usual manner. The Fast Scarlet GG Base, being an exception to the ordinarily used diazotizing procedure, was diazotized by dissolving 1 gm. of the base

---

[1] Trademark.

in about 2 ml. of glacial acetic acid to form a solution which is added with stirring to 31 gm. of a water-ice mixture containing 4.4 ml. of 32% aqueous hydrochloric acid and 0.5 gm. of Triton X–73 (an alkylarylpolyether alcohol). An aqueous solution of 0.59 gm. of sodium nitrite is added to the solution thus obtained. The resulting solution is then stirred for 15 to 30 minutes at a temperature of 35 to 40° F., after which time it is neutralized with 2.5 gm. of sodium acetate.

Tensile strengths of the fibers were determined in the usual manner and any tensile strength relationships given in the examples were based on an average of 10 single-end breaks.

The symbols "g./l." and "cc./l." wherever employed herein designate grams per liter and cubic centimeters per liter, respectively. Temperatures unless otherwise indicated are on the Fahrenheit Scale. Wherever employed herein, the term "fibers" designates fibers regardless of the form they are in, for example, woven or unwoven, and includes fabrics as well as yarns.

Examples 1 Through 6

In each of Examples 1 through 6, a 2 lb. load of 40/2 cotton yarn was placed in a Gaston County Yarn Dyeing Machine (giving a liquor ratio of yarn to dyebath of 1 to 7.5), wetted out with an aqueous wetting solution containing 2 cc./l. wetting agent for 20 minutes at 180° F., rinsed with water and heated to 160° F. An aqueous solution of sodium sulfide flakes (3% based on the weight of yarn) was added to the machine and circulated through the yarn for 10 minutes. A dyebath, 30% SoDyeCo Fast Liquid Black R for Example 1 and 30% SoDyeCo Fast Liquid Black G for Examples 2 through 6, was then added to the machine in two portions. The dyebath was circulated alternately for 7 minutes "outside-in" and for 3 minutes "inside-out," thus providing a 10 minute cycle. The dyebath was circulated in this manner for 20 minutes, after which time 30 g./l. common salt was slowly added on the "outside-in" portion of the cycle. The dyebath was circulated in this manner for an additional 20 minutes, after which time it was removed and a cold running water wash was applied with water entering through the expansion tank, passing through the yarn, and then passing out through the drain. The cold water running wash was continued for 20 minutes.

The dyed yarn in all examples thus treated, was then oxidized by forcing compressed air through the yarn for 10 minutes at room temperature.

The dyed yarns were then treated with the diazotized base or corresponding salt correspondingly listed in Table I, employing the amount of base (in percentages, based on the weight of yarn) as correspondingly listed in said table. The Scarlet GG base was prepared as described above. However, in Examples 1, 2, 4, and 6, no sodium acetate was used in the diazotized base solution. Instead, 1.2% of sulfamic acid was employed to free the diazotized base solution of existing and unused nitrogen to avoid any further oxidation of the dyed yarn. In Example 5, the amount of sodium acetate specified above in the diazotization process was employed. The yarn was rinsed with water and soaped in the usual manner with solution containing 2 g./l. of soda ash and 1 g./l. sodium oleyl taurine (Igepon T–33) at 190° F. for 30 minutes. The yarn was then finally rinsed.

There was obtained in each example a heavy black shade.

The yarn of each example, after the treatment described above, was then tested for bleach fastness and tensile strength. The results of the bleach-fastness tests are listed correspondingly in Table I. The tensile strengths of the yarns were not impaired and compared favorably with yarns dyed in a conventional manner.

TABLE I

Ex.	Diazotized Base Kind or Corresponding Salt	Diazotized Base Amount Percent or Corresponding Salt	Chlorine Bleach Fastness	Peroxide-Bleach Fastness Indicated by Color Loss	Peroxide-Bleach Fastness Indicated by Color Transfer
1	Yellow GC	2.5	good–exc.	good	good–exc.
2	Scarlet GG	3	good–exc.	exc.	good–exc.
3	Scarlet GG Salt.	12(25%)	good–exc.	exc.	good–exc.
4	Orange GC	2.5	good–exc.	exc.	good–exc.
5	Scarlet GG	3	good–exc.	exc.	good–exc.
6	Scarlet GG	3	good–exc.	exc.	good–exc.

In each of Examples 1 through 3, a sample of the dyed yarn, as a control, was removed before oxidation, treated with the diazotized base as described above, rinsed with water, soaped and rinsed again. The tensile strengths of these samples were considerably lower than the tensile strengths of the corresponding air-oxidized, diazotized base-treated yarns. The chlorine- and peroxide-bleach fastness of the control sample was substantially equivalent to that of the air-oxidized, diazotized base-treated yarns.

In each of Examples 5 and 6, a sample of the yarn after oxidation was removed from the machine before the rest of the load was treated with the diazotized base and the sample soaped and rinsed in the manner described above. These samples served as controls and were subjected to the bleaching test and tensile strength test. Each of the control samples lost a considerable depth of shade after chlorine- and hydrogen-peroxide bleaching and bled profusely onto the white cloth wrapping in the hydrogen-peroxide bleach test. The control samples after chlorine bleaching had almost completely lost their original black color. The control samples after hydrogen-peroxide bleaching had lost less color when compared with those subjected to chlorine bleaching, but had bled profusely onto the white cloth wrapping employed in the peroxide bleach tests. The tensile strengths of the control samples were no better than the tensile strengths of the air-oxidized and diazotized base-treated yarn.

Examples 7 Through 9

In order to compare the results obtained by oxidizing the sulfur dyeing with air, with results obtained by oxidizing sulfur dyeings with chemical oxidants, the procedure of Examples 1 through 6 was repeated with the exception that instead of oxidizing with compressed air for 10 minutes at room temperature, the sulfur dyeing was oxidized with 5% sodium perborate for 15 minutes at 140° F. prior to treatment with the diazotized base. Example 7 employed 30% SoDyeCo Fast Liquid Black and Examples 8 and 9 employed 30% SoDyeCo Fast Liquid Black G. Table II below shows the diazotized base or corresponding salt and the amount of diazotized base or salt correspondingly employed in each of Examples 7 through 9. In each example, a sample of yarn was removed after oxidation with the sodium perborate but prior to treatment with the diazotized base. There was obtained in each example a heavy black shade. The yarns obtained in each example and the samples not treated with the diazotized base were tested for chlorine- and hydrogen-peroxide bleach fastness and also for tensile strength. Table II provides the results of the bleach-fastness tests.

TABLE II

Ex.	Diazotized Base Kind	Diazotized Base Amount (Percent)	Bleach Fastness
7	Yellow GC	3.75	poor.
8	Scarlet GG	3.0	poor.
9	Scarlet GG Salt (25%)	12.0	poor.

In every case, the yarn which had been oxidized with the sodium perborate and subsequently treated with the diazotized base had a tensile strength which compared favorably with the tensile strengths of the samples which were removed prior to treatment with the diazotized base. Samples removed prior to treatment with the diazotized base provided substantially similar poor results in the bleach test as the yarns which were treated with the diazotized base after oxidation with sodium perborate.

Examples 10 and 11

These examples show that by oxidizing with potassium bichromate instead of compressed air as an after treatment for the sulfur dye, but prior to treatment with the diazotized base, fails to result in good bleach fastness. In each of Examples 10 and 11, two 10 gm. skeins of 40/2 raw cotton yarn were wetted out at room temperature in an aqueous solution of a synthetic wetting agent in the usual manner. The skeins were then rinsed, squeezed through a wringer to remove excess water and entered into dye-pots having a liquor ratio of 1 part by weight of cotton to 7½ parts by weight of dyebath. The dyebath in each example contained 30% SoDyeCo Fast Liquid Black G. The yarn was dyed with intermittent turning for 20 minutes at 160° F. After this time, 30 g./l. common salt was added and the yarn turned for an additional 20 minutes. Then the yarn was removed, rinsed in tap water and oxidized by immersing it in an aqueous solution, containing 2% potassium bichromate based on the weight of yarn in Example 10, and 4% potassium bichromate in Example 11, for a period of 20 minutes at a temperature of 160° F. The yarn was then removed, rinsed and treated with diazotized Scarlet GG base in the amount of 3% (based on the weight of yarn) for a period of 20 minutes at room temperature. The yarn thus treated was rinsed with cold water, soaped with an aqueous solution containing 2 g./l. of soda ash and 1 g./l. of Igepon T–33 at 200° F. for 30 minutes and finally rinsed with, first hot and then cold water. There was obtained a deep black shade.

The tensile strengths of the yarns thus obtained were found to be unimpaired when compared with yarns treated with the sulfur dye and oxidized with potassium bichromate in the same manner but not treated with the diazotized base. The yarns thus treated, as well as similar yarns not treated with the diazotized base, showed poor fastness to chlorine- and hydrogen-peroxide bleaching.

Example 12

Four 10 gm. skeins of two-ply spun vicose yarn were dyed in the following manner. The skeins were wetted out at room temperature in a conventional wetting agent, rinsed, sqeezed through a wringer to remove excess water, and entered into dye-pots having a liquor ratio of 1 part by weight of yarn to 7.5 parts by weight of dyebath. The dyebath contained 25% SoDyeCo Fast Liquid Black G and 3% sodium sulfide flakes. The skeins were dyed by immersing in the dyebath and intermittently turning them for 20 minutes while maintaining the dyebath at 160° F., then adding 30 g./l. of common salt, and intermittently turning for an additional 20 minutes. The skeins were removed and rinsed in cold water. Skeins 1 and 2 were oxidized by air at room temperature for one hour. Skein 3 was oxidized with a sodium perborate solution containing 5% (based on the weight of yarn) sodium perborate. Skeins 2 and 3 were rinsed with water and entered into a solution containing diazotized 2,5-dichloroaniline in the amount of 3% and sulfamic acid in the amount of 1.2%. Skein 4 was not oxidized after dyeing but was entered directly after rinsing into the diazotized base. Skein 1 was not treated with the diazotized base. All skeins were rinsed with water and soaped in the usual manner. All of the skeins, 1 through 4, carried a deep black shade. Skeins 1 and 3 showed poor fastness to chlorine and peroxide bleaching, turning greenish-gray and gray, respectively, on bleaching with chlorine and badly staining the white cloth wrapper in the peroxide-bleach test. Skein 2 was greatly improved in fastness to chlorine and hydrogen-peroxide bleaching. The tensile strengths of the yarns of skeins 1, 2 and 3 were all of substantially the same high magnitude. The tensile strength of the yarn of skein 4 was considerably lower than that of any of the other skeins.

Examples 13 Through 18

The procedure of dyeing employed in Example 12 for dyeing skein 2 was repeated on cotton yarn. The dyeings thus obtained were air oxidized (with the exception of Example 13, which was not oxidized) at room temperature for the times indicated in the table below. The dyeings thus obtained and oxidized were then treated with the diazotized base as described in Example 12, rinsed with water and soaped in the usual manner. The yarns of all the examples carried a deep black shade. Chlorine-bleach tests, peroxide-bleach tests and tensile strength determinations were made on the yarns thus obtained. The results of the bleach tests are listed correspondingly in the table below.

TABLE III

Ex.	Time (Hrs.)	Chlorine Bleach Fastness	Peroxide-Bleach Fastness Indicated by Color Loss	Peroxide-Bleach Fastness Indicated by Color Transfer
13	0	exc	exc	exc.
14	⅙	exc	exc	exc.
15	½	good	exc	exc.
16	3	good	good	good.
17	24	fair	good	fair.
18	168	poor	good	fair.

The tensile strengths of the yarns of Examples 14 through 18 were of substantially the same high magnitude. The tensile strength of the yarn of Example 13 was, however, considerably lower than those of the yarns in Examples 14 through 18.

Example 19

Employing a procedure similar to that described in Examples 1 through 6, a 2 lb. load of 40/2 cotton yarn was dyed with 25% SoDyeSul Liquid Brown FLCF (Pr. 702 and Sul Red 5), air-oxidized and treated with 3% Scarlet GG Base employing 1.2% sulfamic acid instead of sodium acetate. The yarn, thus dyed, oxidized and treated, when subjected to bleach-fastness tests provided good results.

Yarn dyed in the same manner but oxidized with 5% sodium perborate for 15 minutes at 140° F. instead of air prior to treatment with the diazotized base gave poor results in the bleach-fastness tests. The tensile strengths of the treated, air-oxidized, dyed yarns and the treated, sodium perborate-oxidized dyed yarns were about the same.

A sample of the dyed yarn was removed before oxidation, treated with the diazotized amine and after-treated as described above. The tensile strengths of these unoxidized yarns were considerably lower than the tensile strength of the diazotized amine-treated, air-oxidized, dyed yarns. The bleach-fastness of the unoxidized yarns was substantially equivalent to that of the diazotized amine-treated, air-oxidized, dyed yarns.

Example 20

An approximate 2 lb. load of 40/2 cotton yarn was placed in a Gaston County Yarn Dyeing Machine, wetted out with a solution containing 2 cc./l. wetting agent for twenty minutes at 180° F., rinsed with water and heated to 160° F. An aqueous solution of sodium sulfide flakes (3% based on the weight of yarn) was added to the machine and circulated through the yarn for ten minutes.

A dye solution was prepared by boiling 2½% Sulfogene Brilliant Green J (Concentrated) with 5% sodium sulfide flakes and 2½% soda ash employing about 400 cc. of water. The dye bath was added to the dyeing machine and circulated alternately for seven minutes "outside-in" and for three minutes "inside-out," thus providing a ten minute cycle. The dye bath was circulated in this manner for twenty minutes, after which time 30 g./l. common salt was slowly added on the "outside-in" portion of the cycle. The dye bath was circulated in this manner for an additional twenty minutes, after which time it was removed and a cold running water wash was applied with water entering through the expansion tank, passing through the yarn and then passing out through the drain. The cold water running wash was continued for twenty minutes. The yarn thus treated was then oxidized by forcing compressed air through the yarn for ten minutes at room temperature.

The yarn was then treated with 3% diazotized Fast Scarlet GG Base. The diazotized base was prepared as described above except that 1.2% sulfamic acid was added in place of the sodium acetate used in the above description. The yarn was rinsed with water and soaped in the usual manner with a solution containing 2 g./l. of soda ash and 1 g./l. sodium oleyl taurine (Igepon T–33) at 190° F. for thirty minutes. The yarn was then finally rinsed. The treated yarn after dyeing, oxidizing and treated with the diazotized amine developed a bright deep green shade whereas the untreated yarns, after dyeing and oxidizing, were dull in appearance and somewhat light in shade. As a control, cotton yarn dyed and oxidized but not treated with the diazo base as described above was subjected to bleach fastness and tensile strength tests along with the dyed, oxidized, treated yarns. The chlorine bleach resistance of the untreated yarn was poor whereas the chlorine bleach fastness of the treated yarn was good to excellent. The peroxide bleach fastness of the treated yarn was excellent, having lost little or no color and bleeding to only a slight degree onto its white cloth wrapper. The untreated yarn, however, lost a considerable amount of color and stained its white cloth wrapping severely in the peroxide bleach test. The tensile strengths of both the untreated and treated yarns were of the same general magnitude with the treated yarns being somewhat higher in tensile strength. Unexpectedly, the dyed, oxidized and treated yarn developed an even brighter, deeper green shade after peroxide bleaching than it originally had.

Example 21

Employing the same procedure of dyeing set forth in Example 12, three skeins of cotton yarn were dyed with 20% SoDyeSul Liquid Green NJ. After dyeing and rinsing in cold water, the skeins were treated as follows.

Skein 1 was air oxidized at room temperature for more than an hour, skein 2 was oxidized with air at room temperature for about one hour and then treated with 3% diazotized Scarlet GG Base containing 1.2% sulfamic acid and skein 3 was not air oxidized to any great extent (other than switching the skein from the dyebath to the rinse water and thence to the diazotized amine solution) but was treated with a diazotized amine in the same manner as skein 2. All skeins were rinsed with water and soaped in the usual manner.

Skein 1 developed a dark bluish-green color, skein 2 developed a dark yellowish-green color and skein 3 developed a somewhat lighter yellowish-green color. All skeins were subjected to the bleach fastness test. Skein 1 on chlorine bleaching turned to a light, sky blue color. Skeins 2 and 3 on chlorine bleaching became light green in color with skein 3 being slightly lighter than skein 2. On peroxide bleaching skein 1 turned to a blue shade of moderate depth and severely stained its white cloth wrapping, and skeins 2 and 3 lost some of their original yellowish-green color and only slightly stained their white cloth wrappings. The tensile strengths of all skeins were approximately the same.

The process of the present invention has been described hereinabove with reference to air as the oxidizing medium but it is to be understood that this is for illustrative purposes only and that other oxidizing agents or media are contemplated within the scope of this invention as defined in the appended claims.

What I claim is:

1. An improved method of dyeing cellulosic fibers with Indocarbon black sulfur dyestuff, said fibers having improved fastness to both peroxide and chlorine bleaching without impairment of the tensile strength, comprising the steps of impregnating the fibers with the leuco form of said dyestuff, oxidizing said dyestuff to the intermediate stage of oxidation, treating said fibers with a diazotized amine under substantially non-oxidizing conditions, rinsing the fibers with water, soaping the fibers under alkaline conditions, and thereafter again rinsing the fibers with water.

2. A method as defined in claim 1, and in which the method is carried out in a yarn package dyeing machine and the dyestuff is oxidized to the intermediate stage of oxidation by forcing compressed air through the fibers for 10 minutes at room temperature.

3. Cellulosic textile fibers dyed according to the method defined in claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,874,099	Haller	Aug. 30, 1932
1,879,727	Haller et al.	Sept. 27, 1932
2,280,900	Dreyfus	Apr. 28, 1942
2,344,625	Lubs et al.	Mar. 21, 1944
2,382,188	Vincent et al.	Aug. 14, 1945
2,912,298	Carroll et al.	Nov. 10, 1959