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PROCESS FOR DYEING TEXTILES MADE FROM ACRYLONITRILE-CONTAINING POLYMERS

Archie G. Schoonover, South Charleston, Theophilus A. Feild, Jr., Charleston, and John H. Purse, South Charleston, W. Va., assignors to Union Carbide and Carbon Corporation, a corporation of New York

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4 Claims. (Cl. 8—55)

This invention relates to the dyeing of textile articles formed from or containing filaments or fibers made of acrylonitrile-containing polymers. It has especial utility for the dyeing of articles formed from polyacrylonitriles and from copolymers of acrylonitrile with a wide range of other polymerizable unsaturated compounds containing an olefinic double bond, such as vinyl chloride, vinyl acetate, 2-vinylpyridine, acrylamide, methyl-alpha methacrylate, alphamethacrylamide, and mixtures of such polymers and/or copolymers.

It long has been known that resinous acrylonitrile-containing polymers are highly resistant to dyestuffs and that, as the acrylonitrile content of copolymers of acrylonitrile with such other polymerizable compounds increases, the difficulty of dyeing becomes greater.

In recent years important advances have been made in the art of dyeing articles made from acrylonitrile-containing resinous polymers by a novel and commercially practicable process wherein textile and other articles made therefrom are treated with an aqueous liquid containing a small amount of a compound yielding cuprous ions. This so-called "copper technique" of dyestuff application, which is described in our pending application, Serial No. 217,317, filed March 23, 1951, is believed to represent the first commercially practicable method for dyeing articles made from acrylonitrile-containing resinous polymers to deep shades with acid-type, direct-type and water-soluble acetate-type dyestuffs.

The aforesaid method of dyeing articles made from acrylonitrile-containing polymers which involves the use of cuprous compounds sometimes presents certain dyeing difficulties, resulting in the loss or ineffective use of either or both the costly dyestuff and the copper compound, and an imperfectly dyed article. For example, under certain circumstances during the dyeing operation the cuprous ions, formed from the cupric compound which is introduced in excess into the bath liquid in a soluble almost colorless form at a selected point in the dyeing operation, may change into a finely divided yellow, red or brown oxide powder. The latter may deposit upon the article being dyed and give erratic dyeings. Moreover, depending upon the acid used in the dyeing and the wetting agents employed, one or more of these forms of solid products may exist during the dyeing. While bath temperatures around 212° F. are most favorable for the fixation of the dyestuffs on the article, it is in this temperature range that the reactions forming the insoluble copper oxides and other copper complexes not available for dye fixation also are greatest. The formation of insoluble matter, when it occurs in a dyebath, presents a crocking problem, reduces the effectiveness of the cuprous compounds, and may cause unpredictable dyeing results. The use of an undue excess of the copper compound thus not only is costly but also is detrimental to the uniformity

of the dyeing and to the light-fastness and crock-fastness of the dyed article.

The present invention is based in important part upon the discovery that textiles and other articles formed from or comprising filaments, fibers, yarns and the like made from resinous acrylonitrile-containing polymers may be uniformly and readily dyed to any desired shade of color, using water-soluble dyestuffs of the acid-type, direct-type and/or water-soluble acetate-type, while avoiding at all times the presence in the dyebath of a substantial excess of the copper compound over that required to provide a dyed article of a selected color shade. This is accomplished by initiating the dyeing operation within a dyebath in the substantial absence of a copper compound and thereafter, while the dyeing of the article is continued at temperatures near but substantially below the strain-release temperature at which objectionable change in shape of the article being dyed occurs—and preferably within the range between around 200° F. and around 212° F.—slowly introducing small successive amounts of an aqueous liquid containing cuprous ions, such as those hereinafter described, preferably dropwise, to the dyebath and contents until the desired depth of color is attained in the article being dyed, and then promptly discontinuing the addition of the said aqueous liquid. In this manner material savings of the treating agents are effected. Moreover, various difficulties arising when an undue excess of the copper compound is present in the dyebath at any one time are avoided.

Among the more important objects of the invention are the following: to provide for the dyeing in novel manner of textile and other articles made from or containing acrylonitrile-containing resinous polymers with one or more water-soluble dyestuffs of the acid-type, direct-type and/or water-soluble acetate-type, and mixtures thereof; to provide in novel manner during the dyeing of such articles with said dyestuffs for controlling the rate of exhaustion of the dyestuff and for improving the appearance and color shade of the dyed article; to provide in the dyeing of such articles with said dyestuffs by means of the copper-dyeing technique for minimizing the amount of dyestuff and copper compound required to yield a satisfactorily dyed article of a desired color shade; and to provide, in the dyeing of articles made from acrylonitrile-containing polymers, by processes involving the use of a cuprous compound, for maintaining the copper compound in active available form not injurious to the shade and levelness of the dyeing.

According to one preferred form of the present invention for the dyeing of fibers, yarns and other textile articles made from resinous acrylonitrile-containing polymers, the articles are scoured in known manner with an aqueous solution of a suitable detergent and a wetting agent. The scoured article, after rinsing with water, is placed in an aqueous bath in the ratio by weight of one part of the article to from 10 to 100 parts of water, and commonly in a ratio of around 1:15. One or more water-soluble dyestuffs selected from the class consisting of the acid-type, direct-type and water-soluble acetate-type dyestuffs then is added, with or without a dispersing and leveling agent and/or a swelling and penetrating agent for the resin article. The dyebath temperature then is raised slowly to between 200° F. and the boiling point. Temperatures of 175° F. to 200° F. likewise can be used when a swelling or penetrating agent for the resin also is employed. The dyeing also can be conducted under superatmospheric pressure in an enclosed pressure-tight

vessel at even higher temperatures up to near but below the strain-release temperature of the resin article, i. e., that temperature at which internal strains present in the resin article are released with resultant objectionable change in shape of the article. The dyebath is adjusted, if necessary, to a pH within the range between 2 and 7 as by means of a water-soluble acid. Preferably, sulfuric acid is used, although other mineral acids such as hydrochloric acid and phosphoric acid, and organic acids such as formic acid and acetic acid, can be used.

There then is added slowly to the hot dyebath in successive small increments, preferably dropwise, over a period commonly around 30 minutes, a liquid containing a cuprous compound in a concentration usually ranging from around 0.2% to 2.0% or more, based upon the weight of said liquid, dispersed or dissolved in water. Cuprous sulfate, sulfite, chloride, acetate, formate and the like are useful in the process. It is convenient to use in the process more or less freshly prepared aqueous liquids containing cuprous ions, such as can be made by separately dissolving in water, preferably at room temperature, cupric sulfate or other cupric compound and a reducing agent for the cupric compound in amount required to reduce the latter to the cuprous form—such as the zinc or alkali metal formaldehyde-sulfoxylates, hydroxylamine sulfate, sodium bisulfite, dihydrazine sulfate, glyoxal, and the like—combining the two solutions, and slowly adding portions of the resultant mixture to the hot dyebath.

The dyeing of the article is continued at the aforesaid temperatures, and preferably at around the boiling point of the bath during the slow addition of the treating liquid and until the desired shade of color is secured in the article, or until the dye is exhausted. Additional dyestuff can be added to the bath if and when desired, since in the present process there is never present in the bath such an excess of cuprous compound as to precipitate the dyestuff prematurely or to deposit upon the article. Usually, for best results, the dyeing is conducted for a period of at least one hour at the boiling point of the dyebath. The amount of the cuprous compound—or of the corresponding mixture of cupric compound and reducing agent employed—depends in considerable degree upon the particular acrylonitrile-containing polymer being dyed, the particular dyestuff employed, the depth of color desired, and the temperature and other conditions of the dyeing operation, as will be evidenced from the examples here presented.

The addition to the dyebath of around 40% to 200% or more of an alkali metal sulfate at some stage in the dyeing operation, and commonly after the treating liquid containing the cuprous ions has been added, serves effectively when used to minimize delustering of the article. The dyed article then is scoured at 140° F. in a solution containing a detergent, is rinsed with water, and then is air-dried at temperatures commonly around 160° F. Further relustering may be done, if necessary, by heating the dry dyed article at 240° F.–250° F. with dry heat for a brief period.

In certain forms of the invention, preferred for securing dyeings with deep shades of color on textile articles made from polymers of the foregoing types, and particularly when using dyebath temperatures around 175° F. to 180° F., the dyebath conveniently can have added thereto a dyeing assistant capable of penetrating or swelling the surface of the article. Many swelling or penetrating agents are useful. Particularly effective are derivatives of diphenyl and of benzylphenyl containing one or more hydroxy groups attached to a carbon atom or atoms of an aromatic ring or rings. Such compounds also can contain one to two chlorine atoms attached to a carbon atom or atoms of the same or different aromatic rings. Among suitable compounds are the ortho-, m- and p-phenylphenols, the o,o,'-, o,p'-, and m,m,'-biphenols, p-benzylphenol, p,p'dihydroxydiphenylmethane and the p,p'-dihydroxydichlorodiphenylmethanes. Such swelling agents, when used, can be added to the dyebath conveniently in the form of their alkali metal salts in alkaline solution prior to acidification of the bath. P-phenylphenol, a representative dyeing assistant, is highly effective in proportions around 1% to 15% of the dry weight of the article being dyed. When only medium or light shades of color are desired in the dyeings, a swelling agent for the resin article is not required, and ordinarily is not used.

It often is desirable to have present in the dyebath from 1% to 3% or more of a dispersing and leveling agent, preferably one of the cationic or of the anionic type. Highly effective are the water-soluble cationic products of the condensation of ethylene oxide with an organic amine. Such a product is being marketed under the trade name "Peregal OK." Such products can be made by the process disclosed in United States Patent No. 2,214,352.

The following examples serve to illustrate the invention. In the examples, and throughout the specification and claims, all parts are given in terms of weight, and all percentages are based upon the dry weight of the article being dyed, unless otherwise specified. Each dyebath had a pH within the range from 2 to 7 during the dyeing in the presence of the cuprous compounds.

EXAMPLE 1

A quantity of staple fibers made from a copolymer of acrylonitrile and vinyl chloride containing around 40% of acrylonitrile in the polymer and having a specific viscosity at 20° C. of about 0.26, was scoured in an aqueous solution of a detergent, and then was placed in an aqueous dyebath containing 4% Xylene Milling Blue GL (color index No. 833), 3% of sodium p-phenylphenoxide as penetrating agent, and 1% of "Peregal OK" as leveling agent, and the pH of the dyebath was adjusted to between 4 and 5 with sulfuric acid. The bath was heated to boiling temperature and dyeing proceeded for 30 minutes, after which there was slowly added dropwise to the boiling dyebath during 30 minutes an aqueous liquid containing cuprous ions, and the dyeing continued until the desired color shade was scoured in the fibers. The dyed fibers were scoured and then dried at 250° F.

The treating liquid was made by mixing at room temperature copper sulfate, water, and zinc formaldehyde-sulfoxylate in proportions yielding an aqueous liquid containing 0.25% of copper sulfate and 0.125% of zinc formaldehyde-sulfoxylate, based upon the weight of the liquid. In this dyeing, reduced copper corresponding to 0.82% of cupric sulfate based on the fiber weight was required for maximum dye exhaustion and color depth in the fibers. The dyeing proceeded at an even rate to a medium blue shade.

EXAMPLE 2

Dyeing the same fibers described in Example 1, and following the method described in that example, with the exception that 10% of sodium p-phenylphenoxide was used, and that the dyestuff used was 4% of Anthraquinone Blue SWF 150% Conc., an acid-type of prototype No. 12, and the dyeing was conducted at a maximum dyebath temperature of 175° F., similar results were secured. The dyeing proceeded at an even rate to the desired shade. Cuprous ions corresponding to 4.9% of cupric sulfate were required to give the desired shade of blue.

EXAMPLE 3

Dyeing the same fibers described in Example 1, and following the procedure described in that example, with the exception that the dyestuff used was 4% of Anthraquinone Blue AB (color index No. 1075), and the treating liquid was made by mixing water, cupric sulfate and

hydroxylamine sulfate in proportions to yield a liquid containing 0.25% of cupric sulfate and 0.125% of hydroxylamine sulfate, based upon the weight of the said liquid, cuprous ions corresponding to 2.4% of cupric sulfate were required to give the fibers a good shade of blue. The dyeing proceeded at an even rate to the desired shade.

EXAMPLE 4

Fibers of this kind described in Example 1 were dyed, following the procedure described therein, with the exception that the dyestuff used was 4% of Xylene Milling Navy 4B Conc. (color index No. 304), and the treating liquid containing cuprous ions was made by mixing at room temperature water, cupric sulfate and dihydrazine sulfate in proportions to yield a liquid containing 0.25% of cupric sulfate and 0.125% of dihydrazine sulfate, based upon the weight of the liquid. In the example, 4.2% of cupric sulfate, reduced with 2.1% dihydrazine sulfate, was required to give the fibres the desired good Navy shade. The dyeing proceeded uniformly.

EXAMPLE 5

A quantity of staple fibers of the type described in Example 1 was scoured in an aqueous solution of a detergent. The scoured fibers then were agitated in an aqueous dyebath at a bath to dry fiber weight ratio of 15:1. The bath contained 5% of Cloth Red G (color index No. 249), an acid-type dyestuff, 1.5% of "Peregal OK," and sufficient concentrated sulfuric acid to adjust the dyebath pH to 3.5–4. The dyebath then was brought to a boil, and a treating liquid containing cuprous ions made as hereinafter described, was added dropwise to the boiling dyebath during 30 minutes, and dyeing was continued at the boil for a total of 90 minutes. The dyed fibers then were scoured, and finally dried at 240° F. The fibers were dyed to a good depth of color, and had good wash-fastness and crock-fastness. The color was clear and bright.

In an identical run, with the exception that all of the treating liquid was added to the unheated dyebath at one time prior to being brought to the boil, the dyeing was less clear and bright, and a lighter shade of color was secured.

The treating liquid containing cuprous ions used in this example was prepared by forming an aqueous liquid containing 2% of cupric sulfate and 1% of zinc formaldehydesulfoxylate, based on the weight of the fibers.

EXAMPLE 6

A quantity of staple fibers recited in Example 1, after scouring, was agitated in an aqueous dyebath at a bath to dry fiber weight ratio of 15:1, said bath containing sodium p-phenylphenoxide produced by the reaction of 2.25% of p-phenylphenol and 0.75% of sodium hydroxide. The bath also contained 0.5% of "Peregal OK" as leveling agent. Concentrated sulfuric acid was added until the bath had a pH of 3.5–4 and 5% of Cloth Red G (color index No. 249) then was added. The dyebath was brought to a boil, and a treating liquid containing cuprous ions and made exactly like that described in Example 5 was added dropwise to the hot dyebath during 30 minutes. The dyeing was continued at a boil for a total of 90 minutes. The dyed fibers, after scouring, and then drying at 240° F., were clear and bright, had good color depth, and excellent wash-fastness and crock-fastness.

EXAMPLE 7

A quantity of spun yarn, made from a commercially available acrylonitrile-containing resin believed to contain over 85% and up to 100% of acrylonitrile in the polymer and being marketed under the designation "Orlon Type 41," was scoured, and the said yarn was placed in

a dyebath containing 4% of Xylene Milling Blue GL (color index No. 833), and 1% of "Peregal OK." The pH of the dyebath was reduced to around 4–5, and the dyebath brought to a boil. After 30 minutes at this temperature an aqueous treating liquid containing cuprous ions was slowly added dropwise to the bath during 30 minutes to obtain dyestuff exhaustion. The treating liquid was prepared as a cold aqueous solution containing 0.25% of cupric sulfate and 0.125% of zinc formaldehydesulfoxylate, based upon the weight of the said liquid. Dyeing at the boil was continued until the yarn had attained the desired color shade. In this example, reduced copper ions corresponding to 3.6% of cupric sulfate were required to provide a dyed yarn having the optimum color value. The dyeing proceeded at an even rate to a good blue shade.

EXAMPLE 8

Following the procedure described in Example 7, with the exception that the article dyed was a quantity of spun yarn made from a resinous copolymer of acrylonitrile and vinyl chloride containing around 68% of acrylonitrile in the polymer and having a specific viscosity at 20° C. of 0.41, reduced copper corresponding to 3.1% of cupric sulfate was required to give maximum dyestuff exhaustion and yarn color value. The dyeing proceeded at an even rate to yield the desired blue shade.

EXAMPLE 9

A woven fabric made from continuous filament acrylic fiber being marketed commercially under the trade name "Orlon," and understood to contain 85% or more of acrylonitrile in the polymer, was scoured, and placed in an aqueous dyebath containing 6% of Anthraquinone Blue SWF Conc., 150%. The pH of the bath was adjusted to 5, and the dyebath brought to boiling. After 15 minutes an aqueous treating liquid was slowly added dropwise to the boiling dyebath during a 30 minute period. The treating liquid contained 5% of cupric sulfate and 2.5% of zinc formaldehydesulfoxylate, based upon the fabric weight, dissolved in water at room temperature. After continuing the dyeing at the boil for 45 minutes, the dyed fabric was scoured, and dried at 250° F. It had a good medium shade of color, with good wash-fastness and crock-fastness. The dyestuff exhausted at a uniform rate.

In comparable dyeing where the copper treatment was omitted, only a very faint pastel shade was obtained.

EXAMPLE 10

A woven fabric, made from an acrylic fiber spun from a resinous copolymer of acrylonitrile and vinyl acetate, being marketed under the trade name "Acrilan" and believed to contain around 90% or more acrylonitrile in the polymer, was scoured and then placed in an aqueous dyebath containing 2% of "Peregal OK," 4% of Anthraquinone Blue SWF Conc., 150%, 6% of sodium p-phenylphenoxide, and enough sulfuric acid to adjust the pH to 5. The dyebath was brought to a boil. After 15 minutes an aqueous treating liquid was slowly added dropwise to the bath during 30 minutes. The treating liquid was prepared by dissolving 5% of cupric sulfate and 2.5% of zinc formaldehydesulfoxylate, based upon the fabric weight, in water at room temperature to form an aqueous solution containing about 1.0% of cupric sulfate, based upon the weight of said liquid. The dyeing then was continued at the boil for 45 minutes. The dyed fabric was scoured, and dried at 250° F. It had a medium shade of blue, and good wash-fastness and crock-fastness. The dyestuff exhausted at an even rate. In comparable dyeings where the copper-containing treating liquid was not used, only a pastel color shade was obtained.

Among the many dyestuffs useful in the process are the following:

Acid-type dyestuffs

Trade name:	Color index No.
Xylene Milling Blue BL	833
Vitrolan Orange R. Conc	Pr. 146
Xylene Milling Yellow P	------
Xylene Milling Yellow 2GP	------
Xylene Fast Red 2GP	------
Xylene Light Rubine 2GS	------
Calcoid Neutral Brown RS	------
Anthralan Red BA–CF	Pr. 210
Chromaven Milling Orange G. Conc	274
Alizarine Light Brown BL	------
Alizarine Light Green GSN	------
Alizarine Light Gray RLL	------
Alizarine Light Red R	------
Alizarine Sky Blue BS–CF	1088
Alizarine Cyanine Green GHN–CF	1078
Brilliant Alizarine Light Red 4B	------
Sulfonine Red G	430
Calcochrome Alizarine Gray 2BLS	Pr. 206
Xylene Fast Rubine 3GP	Pr. 412
Amacid Red 3B Conc	208
Sulfonine Orange GS	Pr. 151
Sulfonine Yellow 2G	642
Cloth Red G	249
Croceine Scarlet MOO	252
Anthraquinone Violet R	1080
Anthraquinone Blue SWF 150%	Pr. 12
Supramine Yellow 3GLA–CF	Pr. 474
Calcocid Milling Red 3R Conc	275

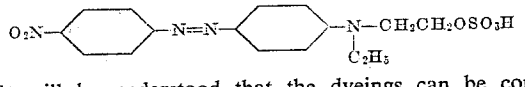
Direct-type dyestuffs

Trade Name:	Color index No.
Calcomine Brilliant Yellow Conc	365
Fastusol Brown LBR	---
Fastusol Red 4BA	278
Calcodur Yellow BL Conc	814
Calcodur Yellow NN	814

Water-soluble acetate-type dyestuffs

Trade Name:	Color index No.
Solacet Fast Violet RS	---
Solacet Fast Yellow GS	---
Solacet Fast Scarlet B–125 [1]	---
Solacet Fast Green 2GS	---
Solacet Fast Blue 2BS	---
Solacet Fast Orange 2GKS	---
Solacet Fast Red 5BGS	---

[1] This dyestuff has the structure:



It will be understood that the dyeings can be conducted at temperatures above the boiling temperature of the dyebath in pressure-tight vats under corresponding pressures, providing that the temperature is at least below the strain-release temperature of the fiber—that temperature at which internal strains present within the article are released sufficiently to cause objectionable change in shape of the article. Variations in the order of procedure of adding to the dyebath the various components, other than the copper-containing agent and the reducing agent therefore, can be made without departing from the invention. The swelling agent, when used, can be added to the bath from a solution thereof in a suitable solvent, or it may be added in the form of a micronized powder.

The specific viscosities of the resins referred to herein were determined at 20° C. using an Ostwald viscosimeter in accordance with the formula:

$$\text{Specific viscosity} = \frac{\text{Viscosity of a solution of 0.1 gram of the resin in 50 cc. of solvent}}{\text{Viscosity of the solvent}} - 1$$

In determining these specific viscosities, cyclohexanone was used with the resins of Examples 1 to 6, and dimethylformamide was used with the resin of Example 8. The specific viscosity of the resin is a direct function of its average molecular weight.

This application is a continuation-in-part of our pending application, Serial No. 217,317, filed March 23, 1951.

The invention is susceptible of modification within the scope of the appended claims.

We claim:

1. Process for dyeing textile articles made from polyacrylonitriles and copolymers of acrylonitrile with at least one other polymerizable compound containing a single olefinic double bond, which comprises treating such an article with an aqueous dyebath having a pH within the range from 2.0 to 7.0 and containing a water-soluble dyestuff selected from the class consisting of the acid-type, direct-type and water-soluble acetate-type dyestuffs, and slowly adding to said aqueous dyebath successive small amounts of a compound yielding cuprous ions while heating the article in the dyebath containing cuprous ions at a temperature of at least 175° F. for at least 15 minutes.

2. Process for dyeing textile articles made from resinous polyacrylonitriles and copolymers of acrylonitrile with at least one other polymerizable compound containing a single olefinic double bond with water-soluble dyestuffs in the presence of sufficient cuprous ions to provide ready exhaustion of the dyestuff, while minimizing the amount of copper compound required to produce a dyed article of selected color shade, which comprises treating such an article with an aqueous dyebath having a pH within the range from 2 to 7 and containing a water-soluble dyestuff selected from the class consisting of the acid-type, direct-type and water-soluble acetate-type dyestuffs, and slowly adding to such dyebath during a period of at least 10 minutes successive small amounts of an aqueous solution of a copper compound yielding cuprous ions while heating the article in the dyebath at a temperature of at least 175° F., and discontinuing the slow addition of the copper compound to the solution when the article has attained approximately the desired shade of color.

3. Process for dyeing textile articles made from resinous polyacrylonitriles and copolymers of acrylonitrile with at least one other polymerizable compound containing a single olefinic double bond with water-soluble dyestuffs in the presence of sufficient cuprous ions to provide ready exhaustion of the dyestuff, while minimizing the amount of copper compound required to produce a dyed article of selected color shade, which comprises treating such an article with an aqueous dyebath having a pH within the range from 2 to 7 and containing a water-soluble dyestuff selected from the class consisting of the acid-type, direct-type and water-soluble acetate-type dyestuffs, and slowly adding to such dyebath during a period of at least 10 minutes, successive small increments of an aqueous solution containing a copper compound yielding cuprous ions, while heating the article in the dyebath at a temperature of at least 200° F., and discontinuing the addition of the solution of the copper compound to the dyebath when the article has attained approximately the desired shade of color.

4. Process for dyeing textile articles made from resinous polyacrylonitriles and copolymers of acrylonitrile with at least one other polymerizable compound containing a single olefinic double bond with water-soluble dyestuffs in the presence of sufficient cuprous ions to provide ready exhaustion of the dyestuff, while minimizing the amount of copper compound required to produce a dyed article of selected color shade, which comprises treating such an article with an aqueous dyebath having a pH within the range from 2 to 7 and containing a water-soluble dyestuff selected from the class consisting of the acid-type, direct-type and water-soluble acetate-type dyestuffs, together with a swelling agent for the resin, and slowly adding to such dyebath during a period of at least 10 minutes suc-

cessive small increments of an aqueous solution containing a cupric compound and a reducing agent for the latter yielding cuprous ions, while heating the article in the dyebath at a temperature of at least 175° F., and discontinuing the addition of the solution of the copper compound to the dyebath when the said article has attained approximately the desired shade of color.

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