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DYEING TEXTILE MATERIALS MADE FROM
VINYL HALIDE-ACRYLONITRILE RESINS
AT HIGH TEMPERATURES IN THE PRESENCE OF MOISTURE

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This invention relates to the dyeing of textile fibers, filaments and yarns, and woven, knitted, braided, felted and other textile articles, made from certain thermoplastic resins. More especially, it concerns a process for dyeing textile articles made from or containing vinyl resins produced by the copolymerization of a vinyl halide with acrylonitrile.

The invention is particularly useful for the dyeing of textile articles made from acetone-soluble resinous copolymers of vinyl chloride and acrylonitrile having between about 45% and about 80% of the chloride in the polymer, and having specific viscosities at 20° C. between 1.5 and 6.0. Furthermore, the invention has especial utility for the dyeing of textile articles made from such vinyl chloride-acrylonitrile copolymers wherein the fiber or yarn, after its production, has been stretched at elevated temperatures around 105° C. to 150° C., and the stretched yarn then has been rendered dimensionally stable at 100° C. in water, against more than a few per cent shrinkage in water or steam at temperatures up to around 120° C. and is partially or wholly resistant to acetone and various volatile spinning solvents.

Filaments and yarns made from vinyl chloride-acrylonitrile copolymer resins readily are dyed in water with most of the acetate-type dyestuffs at temperatures between 95° C. and 100° C. Most of the other types of dyestuffs have very low or no affinity for the yarn and either do not dye the yarn at all or else produce only very light shades or tints under the usual dyeing conditions.

In the dyeing of textile articles it is highly desirable to be able to use different types of dyestuffs in order to obtain the wide variety of effects and fastness qualities demanded. The vinyl chloride-acrylonitrile resin yarns have very low affinity for most of the acid-type colors. The basic-type, direct-type and phthalic anhydride-type colors, although easily applied to the yarn, have very poor wash and crock fastness. It now has been found that although these colors have low dye affinity or poor fastness properties when applied by the normal dyeing procedures, excellent fastness qualities and high affinity can be obtained when these colors are applied from aqueous dyebaths at elevated temperatures, or when they are applied from moderate temperature treating baths, and then are fixed in the coated article by a heat treatment as hereinafter described at an elevated temperature of at least 105° C. in the presence of moisture—e. g., steam under pressure.

Among the more important objects of the invention are the following: to provide for improving the affinity of fibers, yarns and other textile articles made of vinyl halide-acrylonitrile

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copolymer resins for dyestuffs which, under normal dyeing conditions, yield very little or no color depth and which articles do not retain the color upon washing; to provide for producing from textile articles made from vinyl chloride-acrylonitrile copolymer resins dyed articles of excellent color depth and wash fastness by the use of acid-type, basic-type, direct-type and phthalic anhydride-type dyestuffs; to provide for the dyeing with the aforesaid dyestuffs of stretched fibers and yarns made from a vinyl halide-acrylonitrile copolymer resin, and fabrics and other textile articles made from such stretched fibers and yarns, while minimizing or substantially preventing shrinkage of the stretched fibers or yarns and retaining their orientation and tensile strengths at elevated temperatures around 120° C. These and other objects will be evident from the following description of the invention.

In accordance with this invention, fibers and yarns made from a resinous copolymer of a vinyl halide and acrylonitrile, and textile fabrics containing such fibers and yarns, are immersed, preferably with agitation, in an aqueous dyebath containing a small amount of a dyestuff, such as an acid-type, basic-type, direct-type or phthalic anhydride-type dyestuff.

Particularly good results are secured when the textiles are made from copolymers of vinyl chloride and acrylonitrile having between around 45% and around 80% of the chloride in the polymer and having specific viscosities at 20° C. of between 1.5 and 6.0. This is especially true where the textiles are made from or contain fibers or yarns which, after their production, have been stretched at elevated temperatures around 105° C. to 150° C. and the stretched yarn then has been rendered dimensionally stable by heating in water or steam at temperatures around 100° C. to 120° C. while untensioned, or has been rendered dimensionally stable and acetone-resistant by heating the stretched yarn with dry heat at temperatures between about 135° C. and about 175° C. for from two minutes to four hours while under tension sufficient to prevent substantial shrinkage of the yarn, whereby the yarn is stabilized against more than a few per cent of shrinkage at temperatures up to around 120° C., and is rendered partially or wholly insoluble in acetone.

Processes for making such dimensionally stable textile articles are disclosed in United States Patent No. 2,420,565, of E. W. Rugeley, T. A. Feild, Jr., and J. L. Petrokubi, and in the United States Patent No. 2,499,477, of T. A. Feild, Jr., respectively.

The specific viscosities referred to herein are

determined at 20° C. using an Ostwald viscometer, in accordance with the formula:

$$\text{Sp. viz.} = \frac{\text{Viscosity of a solution of 0.1 gram of the resin in 50 cc. acetonyl acetone}}{\text{Viscosity of the acetonyl acetone}} - 1$$

The dyebath commonly contains a small amount of a water-soluble soap and a water-softening agent preventing the precipitation of water-insoluble compounds. Such an agent is a sodium phosphate glass being marketed under the trade-name "Calgon." Other agents include the alkali metal salts of sulfuric acid esters having at least eight carbon atoms. After the bath reaches the selected temperature, preferably around 100° C., a few per cent of sodium sulfate conveniently may be added to improve the exhaustion of the dye.

The dyebath usually contains between 1% and 5% of the dye, although lesser and larger amounts of the dye may be used.

In dyeing the vinyl halide-acrylonitrile yarns and other textile articles in accordance with the process, such articles are immersed in the dyebath, preferably with agitation. When the dyebath is at a temperature of around 90° C. to 100° C. a period of exposure of from five to ten minutes is particularly effective. Longer times of exposure may be employed, especially when using dyebaths at lower temperatures, as exemplified in Example VII.

Following the initial dye-applying operation, the coated yarn or other article is subjected to moist heat at temperatures within the range from 105° C. to around 150° C., for a period of from around thirty minutes to two hours or more, the time of treatment varying inversely with the temperature and pressure used. This serves to insure uniform fixation of the dye in the yarn, and to provide dyeings of excellent color depth and wash fastness. Temperatures of from 105° C. to 125° C. are employed when the heating is done in the presence of water or steam under superatmospheric pressure—e. g., three to nineteen pounds per square inch, gauge—while temperatures of from around 125° C. to around 150° C. are used when heating under atmospheric pressure in the presence of superheated steam or of air containing superheated steam in amount sufficient to humidify the air.

When fixing the color in dimensionally-stabilized and/or heat-modified textile articles of the aforesaid types the temperature employed preferably is not substantially higher than the maximum temperature at which the undyed textile article is substantially dimensionally stable in moist heat, or at which it has a shrinkage of not more than about 5%.

This high temperature color-fixation step may be conducted in various ways. Thus, it may be applied to the dyed article while the latter is immersed in the dyebath; or after removal of the article from the dyebath and draining of the excess dye liquor. The heat treatment advantageously may be applied after removal of the article from the dyebath, while in a current of circulating air maintained under atmospheric pressure and at temperatures ranging between around 125° C. and around 150° C., and containing steam in amount sufficient to humidify the air. Both the initial dye-applying step and the subsequent high temperature dye-fixation and development step essentially are conducted in the presence of moisture. The use of dry heat, at the temperatures used in the fixation step, fails to provide the desired improvement either in the color

development on the resin articles or in the color fastness of the dyed article.

The improvement in the affinity of the dye-stuff for the vinyl halide-acrylonitrile copolymer textile and in the color fastness becomes marked in yarns dyed and fixed at 110° C. or above, or treated with the dye at lower temperatures and then subjected to the fixing heat treatment at 110° C. or above, although improvement is noted at temperatures as low as 105° C.

The maximum temperature useful for fixing the dye in these yarns and fabrics is limited to the amount of shrinkage which can be tolerated. The invention has outstanding utility in connection with the dyeing of textile articles made from vinyl chloride-acrylonitrile copolymer resins, which textiles have been rendered dimensionally stable against substantial shrinkage at temperatures up to around 120° C. Such articles have their acetone solubilities greatly reduced and have increased affinities for the dyestuffs. Thus, high tenacity stretched yarns made of vinyl halide-acrylonitrile copolymer resins, which yarns have been subjected to a heat-modification treatment by exposure to dry heat at temperatures of from 135° C. to 175° C. for periods of from two minutes to four hours while under tension sufficient to prevent shrinkage, and fabrics made from such yarns, are dimensionally stable at elevated temperatures and readily are dyed by the process to excellent full shades with little or no shrinkage of the dyed stretched yarn at elevated temperatures of 120° C. or less in steam or water under pressure, or at temperatures up to around 150° C. in air containing moisture or in steam at atmospheric pressure. Yarns not thus heat-modified shrink somewhat more at 120° C., and have a somewhat lower affinity for the dyestuffs.

In the dye-fixing step, the difference between the action of steam and hot water under pressure upon the aforesaid dimensionally stable articles and the action thereon of hot humidified air at atmospheric pressure is quite pronounced. When using steam or hot water under pressure such an article retains its dimensional stability only when employing dye-fixing temperatures up to about 125° C., whereas when using hot circulating air humidified with superheated steam at atmospheric pressure the dimensional stability of the textile article is substantially retained at temperatures as high as about 150° C. However, humidified circulating air cannot effectively be used in the dye-fixing step at temperatures below about 125° C. On the other hand, when using steam or hot water under pressure at temperatures above around 125° C., excessive shrinkage of the dimensionally stable textile article often occurs.

In general the most desirable results are obtained with stretched heat-modified yarns and fabrics, although excellent results are obtained when applying the process to unstretched and unstabilized staple fibers and yarns of the vinyl halide-acrylonitrile resins; and good results are secured when stretched yarns of this type of resin are exposed, prior to the dyeing operation, to moist heat at temperatures of around 100° C.-120° C. for at least one hour while untensioned, and thus are dimensionally stabilized against shrinkage at temperatures of at least 100° C. When dyeing unstretched and dimensionally unstabilized yarns and fibers, more shrinkage can be tolerated than in the case of fabricated textile articles.

The effectiveness of the process is surprising in view of the fact that the affinity of these articles for dyes of the types mentioned herein, and the fastness of the dyes in such articles, are not improved by a pretreatment of the yarn with steam under pressure at elevated temperatures of around 105° C. to 120° C., followed by the dyeing of the yarn at normal dyeing temperatures up to 100° C. Furthermore, the use of dry heat in the dye-fixation step of the process does not improve the dye-fixation in these articles.

Among the dyestuffs found to be particularly suitable for dyeing vinyl halide-acrylonitrile resin articles in accordance with the invention, and which have good affinity for textiles made from these resins and excellent fastness to washing and crocking, are the following:

Acid-type dyestuffs

Calcocid Milling Red 3R Conc., C. I. 275, Calco Chemical Div. of American Cyanamid Corp.
Calcocid Violet 4BX, C. I. 698, Calco Chemical Div. of American Cyanamid Corp.
Calcocid Yellow BN, C. I. 146, Calco Chemical Div. of American Cyanamid Corp.
Calcocid Yellow JY, Calco Chemical Div. of American Cyanamid Corp.
Du Pont Nigrosine WSJ Powder, C. I. 865, E. I. du Pont de Nemours & Co.
Du Pont Resorcin Brown 5G, E. I. du Pont de Nemours & Co.
Ciba Scarlet 2R, C. I. 79, Ciba Co.
Alizarine Direct Blue ARA, P. R. 11, General Dyestuffs Corp.
Alizarine Irisol RD, General Dyestuffs Corp.
Indian Yellow GA, General Dyestuffs Corp.
National Wool Violet 4BN, C. I. 698, National Aniline & Chemical Co.
National Fast Acid Brown RG, National Aniline & Chemical Co.

Direct-type dyestuffs

Calcomine Scarlet 3B, C. I. 382, Calco Chemical Div. of American Cyanamid Corp.
Calcomine Dark Green BG Conc., C. I. 583, Calco Chemical Div. of American Cyanamid Corp.
Calcomine Catechu 4G, P. R. 70, Calco Chemical Div. of American Cyanamid Corp.
Calcomine Orange GG Conc., Calco Chemical Div. of American Cyanamid Corp.
Calcomine Brown MP, Calco Chemical Div. of American Cyanamid Corp.
Calcomine Black Ex. Conc., C. I. 581, Calco Chemical Div. of American Cyanamid Corp.
Calcodur Yellow NN, C. I. 814, Calco Chemical Div. of American Cyanamid Corp.

Basic-type dyestuffs

Bismark Brown RRN Conc., General Dyestuffs Corp.
Victoria Blue BA Conc., General Dyestuffs Corp.
Auramine DO Conc., C. I. 655, General Dyestuffs Corp.
Du Pont Victoria Green SC, C. I. 657, E. I. du Pont de Nemours & Co.

Phthalic anhydride-type dyestuffs

Rhodamine B ex., C. I. 749, General Dyestuffs Corp.
Astra Philoxine, General Dyestuffs Corp.

The following examples further serve to illustrate the invention. In the examples the amount of dyestuff used is expressed in terms of per cent by weight of the article being dyed. A dyebath to article weight ratio of about 30:1 was used.

Example I

A tube knit fabric made from oriented 70-denier heat-modified yarns of a vinyl chloride-acrylonitrile copolymer resin having a vinyl chloride content of 60.3%, and a specific viscosity at 20° C. of 0.3, was immersed for ten minutes in a boiling aqueous dyebath containing 1% by weight of Calcocid Milling Red 3 R Conc. and about 2% of sodium sulfate. The dyebath temperature then was increased to 120° C. and maintained for two hours under pressure. The resultant article was dyed to a full red shade; and the dyed fabric was very fast to a boiling soap solution, and showed no crocking. When attempting to dye the fabric in the boiling dyebath, only a very weak shade was obtained.

The stretched yarns forming the knit fabric had been heat-modified to inhibit or minimize shrinkage at temperatures around 100° C. to 125° C. in steam by heating the stretched yarn for three hours at a temperature of about 135° C. while the yarn was untensioned.

Example II

A quantity of the tube knit fabric described in Example I was immersed for ten minutes in a boiling aqueous dyebath containing 4% by weight of Calcocid Violet 4BX and a small amount of sodium sulfate to improve exhaustion of the dyebath. Thereafter separate portions of the fabric and of the dyebath were heated under pressure at temperatures, respectively, of 108° C., 115° C., and 120° C., for a two hour period to fix the colors in the fabric. The depth of color in the dyed fabric increased with increase of the fixing temperature, and ranged from a full medium violet to a deep violet. The colors had excellent wash and crock fastness. The same yarn, when dyed at a boil only, had a light medium shade.

Example III

A quantity of the tube knit fabric described in Example I was immersed for ten minutes in a boiling aqueous solution containing 1% by weight of du Pont Victoria Green SC dye. Following this treatment the color was evenly distributed on the fabric. However, the color had very poor resistance to scouring, and crocked badly.

The fabric again was immersed in the boiling dye-bath, and the fabric and bath were heated to 120° C. for two hours in an autoclave under pressure. The resultant fabric was dyed a deep brilliant green shade which was fast to boiling soap solution and showed no crocking.

Example IV

A quantity of the tube knit fabric described in Example I was coated with the same dye and in the same manner described in that example. After the treatment in the boiling dyebath the fabric was removed therefrom, excess dye liquor drained off, and the moist fabric heated in an autoclave at 120° C. under pressure for two hours. A full red shade was secured with excellent fastness to washing.

Example V

Three-inch staple lengths of unstretched fibers made from a vinyl chloride-acrylonitrile copolymer resin containing 59.8% of the chloride in the polymer and having a specific viscosity at 20° C. of 0.4, were immersed for ten minutes in an aqueous dyebath heated to 100° C. and containing 4% by weight of Alizarine Irisol RD, and traces of a water-soluble soap and of "Calgon." Thereafter the dyebath temperature was increased to 120° C.,

and maintained under pressure at this temperature for two hours without agitation of the fibers immersed therein. The resultant staple fibers were very crinkly, and were uniformly dyed—although this color showed no affinity for the fibers at dyebath temperatures of 100° C. The fastness qualities of the dyed articles were very good. The depth of color secured was lower than that obtained by dyeing under equivalent conditions stretched yarns that had been heat-modified at temperatures above 120° C.

When substituting in the process for the unstretched fibers other fibers and yarns that have been stretched and then heat-modified at temperatures of at least 120° C. while under tension preventing shrinkage, the dyed products are relatively free from crinkle but are less soluble or are insoluble in acetone.

Example VI

A tube knit fabric was prepared from 70-denier stretched and heat-modified yarn made from a vinyl chloride-acrylonitrile copolymer resin having 60.3% of the chloride in the polymer and having a specific viscosity at 20° C. of around 0.3. The yarn had been stretched 1500% and the stretched yarn heat-modified by heating it for three hours at a temperature of 135° C. while untensioned.

This fabric, untensioned, was immersed for twenty minutes in a boiling aqueous treating bath containing 4% by weight of Calcoacid Violet 4BX. The treated fabric then was removed from the bath, drained, and placed for thirty minutes in an oven heated to 150° C. in which air under atmospheric pressure was circulated, while live steam was bled into the oven to humidify the air. The resultant fabric was dyed a deep violet. The wash and crock fastness characteristics of the dyeings were very good. Little if any shrinkage of the fabric occurred as a result of the dyeing operation.

Example VII

A tube knit fabric was prepared from a 100-denier yarn made from a vinyl chloride-acrylonitrile copolymer resin having 60.3% of the chloride in the polymer and a specific viscosity at 20° C. of 0.4. The yarn had been stretched 1289% at 119° C., and the stretched yarn had been heat-modified and rendered dimensionally stable by heating for two hours at 150° C. while under tension sufficient to prevent shrinkage.

This fabric was immersed for fifteen minutes, untensioned, in an aqueous bath maintained at 60° C. and containing 4% Calcoacid Violet 4BX and 0.3% of acetic acid. After the dye-applying treatment to obtain level distribution of the dyestuff on the surface of the yarn the dyebath and fabric were heated for one hour at 120° C. in an autoclave under pressure, thereby fixing the dye in the fabric. The dyed fabric then was removed and scoured in the usual manner.

Although the fabric, following application of the dyestuff at 60° C. was uniformly coated with the dyestuff, the latter readily was removed by a light rinse. After the dye-fixing treatment a full violet shade was obtained which was fast to washing and crocking. The dyed fabric was dimensionally stable against substantial shrinkage in moist heat at temperatures as high as 120° C.

The term "hot water" as used in the claims is intended to include the aqueous dyebath. Such dyebaths usually contain, in addition to the

water, small amounts of the dye and other ingredients, as recited herein.

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

We claim:

1. Process for improving the wash fastness and crock fastness of filaments, yarns, fabrics and other textile articles made from a vinyl halide-acrylonitrile copolymer resin which has been treated with a dyestuff for which such resin has a low affinity, which comprises heating such textile article at an elevated temperature in the presence of moisture and under a pressure ranging from atmospheric pressure to around twenty pounds per square inch, said temperatures being within the range from 105° C. to around 125° C. when the moisture is under superatmospheric pressure in the form of at least one member of the class consisting of steam and hot water, and ranging from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, thereby providing a dyed article of excellent wash fastness and crock fastness.

2. Process for improving the wash fastness and crock fastness of dyed filaments, yarns, fabrics and other textile articles made from a vinyl halide-acrylonitrile copolymer resin which has been treated with an acid-type dyestuff at a temperature not substantially higher than 100° C., which comprises heating such treated textile article at an elevated temperature in the presence of moisture and under a pressure ranging from atmospheric pressure to around twenty pounds per square inch, gauge, said temperature ranging from 105° C. to around 125° C. when the moisture is in the form of at least one member of the class consisting of steam and hot water under superatmospheric pressure and ranging from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness.

3. Process as defined in claim 1, wherein the dyestuff is a direct-type dyestuff.

4. Process as defined in claim 1, wherein the dyestuff is a basic-type dyestuff.

5. Process for improving the wash fastness and crock fastness of dimensionally stable filaments, yarns, fabrics and other textile articles made from a vinyl halide-acrylonitrile copolymer resin which have been treated with a dyestuff for which such resin has a low affinity, while preserving the dimensional stability of the undyed article, which comprises heating such treated, dimensionally stable textile article at an elevated temperature in the presence of moisture and under a pressure within the range between atmospheric pressure and around twenty pounds per square inch, said temperature being within the range from 105° C. to around 125° C. when the moisture is in the form of at least one member of the class consisting of steam and hot water and is under a superatmospheric pressure corresponding to such temperature, and being within the range from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, and such temperature being not substantially higher than the maximum temperature at which the undyed textile article is dimensionally stable, thereby

providing a dyed article of excellent wash fastness and crock fastness in which the dimensional stability of the undyed article has been preserved.

6. Process for dyeing textile articles comprising stretched, dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of a dyestuff for which such resin has a low affinity, while retaining such dimensional stability in the dyed article which comprises coating the textile article with such a dyestuff at a temperature not substantially higher than 100° C., and thereafter further heating the coated textile article at an elevated temperature in the presence of moisture while under a pressure ranging from atmospheric pressure to around twenty pounds per square inch, gauge, said temperature ranging from 105° C. to around 125° C. when the moisture is in the form of at least one member of the class consisting of steam and hot water under superatmospheric pressure corresponding to such temperature, and ranging from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability at elevated temperatures of the undyed article has been preserved.

7. Process as defined in claim 6, wherein the dyestuff is an acid-type dyestuff.

8. Process as defined in claim 1, wherein the dyestuff is a direct-type dyestuff.

9. Process for dyeing textile articles comprising stretched, dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff, while retaining such dimensional stability in the dyed article which comprises immersing said textile article for at least five minutes in a treating bath containing such dyestuff and maintained at a temperature between around 60° C. and around 100° C., and thereafter further heating the textile article at an elevated temperature in the presence of moisture while under a pressure ranging from atmospheric pressure to around twenty pounds per square inch, gauge, said temperature ranging from 105° C. to around 125° C. when the moisture is in the form of at least one member of the class consisting of steam and hot water under superatmospheric pressure corresponding to such temperature, and ranging from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability at elevated temperatures of the undyed article has been preserved.

10. Process for dyeing textile articles comprising stretched, dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff, while retaining such dimensional stability in the dyed article which comprises immersing said textile article for at least five minutes in an aqueous treating bath containing such a dyestuff and maintained at a temperature between around 60° C. and around 100° C., and thereafter further heating the textile article under superatmospheric pressure at a temperature within the range from 105° C. to around 125° C. for a period of between thirty minutes to two hours while immersed in said bath, the time of heating varying inversely with the temperature, thereby

providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability at elevated temperatures of the undyed article has been preserved.

11. Process for improving the wash fastness and crock fastness of dimensionally stable filaments, yarns, fabrics and other textile articles that are dimensionally stable up to at least 100° C., and are made from a vinyl halide-acrylonitrile copolymer resin which have been treated with an acid-type dyestuff at an elevated temperature, while preserving the dimensional stability of the undyed article, which comprises heating such treated dimensionally stable textile article for a period of from thirty minutes to two hours at an elevated temperature in the presence of moisture and under a pressure ranging from atmospheric pressure to around twenty pounds per square inch, gauge, said temperature being within the range from 105° C. to around 125° C. when the moisture is in the form of at least one member of the class consisting of steam and hot water under superatmospheric pressure, and being within the range from around 125° C. to 150° C. when the moisture is in the form of superheated steam at atmospheric pressure, the time of heating varying inversely with the temperature, and such temperature being not substantially higher than the maximum temperature at which the undyed textile article is dimensionally stable, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability of the undyed article has been preserved.

12. Process for dyeing textile articles comprising substantially dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff while preserving the dimensional stability of the undyed article, which comprises immersing such a textile article for at least five minutes in a treating bath containing such a dyestuff and maintained at a temperature between around 60° C. and around 100° C., and thereafter further heating such treated textile article at a temperature within the range between 105° C. and around 125° C. for a period of between thirty minutes and two hours in the presence of water under pressure, the time of heating varying inversely with the temperature, said temperature being not substantially higher than the maximum temperature at which the undyed article is dimensionally stable, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability of the undyed article has been preserved.

13. Process for dyeing textile articles comprising substantially dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff while preserving the dimensional stability of the undyed article, which comprises immersing such a textile article for at least five minutes in an aqueous treating bath containing such a dyestuff and maintained at a temperature between around 60° C. and around 100° C., and thereafter further heating the textile article under superatmospheric pressure at a temperature within the range from 105° C. to around 125° C. for a period of between thirty minutes and two hours while immersed in said bath, the time of heating varying inversely with the temperature, and the temperature being not substantially higher than the maximum temperature at which the undyed

textile article is dimensionally stable, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability of the undyed article has been preserved.

14. Process for dyeing textile articles comprising substantially dimensionally stable filaments, fibers or yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff while preserving the dimensional stability of the undyed article, which comprises immersing such a dimensionally stable textile article for at least five minutes in a treating bath containing such a dyestuff and maintained at a temperature between around 60° C. and around 100° C., and thereafter further heating the textile article under atmospheric pressure at a temperature within the range from around 125° C. to around 150° C. for a period of between thirty minutes and two hours in the presence of hot circulating air containing superheated steam, the time of heating varying inversely with the temperature, and the temperature being not substantially higher than the maximum temperature at which the undyed textile article is dimensionally stable, thereby providing a dyed article of good color depth and excellent wash fastness and crock fastness in which the dimensional stability of the undyed article has been substantially preserved.

15. Process for dyeing textile articles comprising stretched dimensionally stable filaments, fibers and yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff to provide a dyeing of good color depth and wash fastness, while minimizing loss in stability of the stretched filaments, fibers and yarns, which comprises immersing for between five minutes and thirty minutes in an aqueous treating bath containing such a dyestuff and heated to between around 60° C. and 100° C., a textile article comprising stretched dimensionally stabilized filaments, fibers or yarns of a vinyl halide-acrylonitrile resin which are resistant to shrinkage at temperatures around 100° C. to 120° C. in steam under pressure in the untensioned condition, and thereafter heating the thus treated article while untensioned at a temperature between around 110° C. and around 120° C. in the presence of water under pressure for a period of from thirty minutes to two hours, thereby providing a dimensionally stable dyed textile article of good color depth and excellent wash fastness and crock fastness.

16. Process for dyeing textile articles comprising stretched dimensionally stable filaments, fibers and yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff to provide a dyeing of good color depth and wash fastness while substantially preserving the dimensional stability of the dyed filaments, fibers and yarns, which comprises immersing for between five minutes and thirty minutes in an aqueous treating bath containing such a dyestuff and heated to between around 60° C. and 100° C., a textile article comprising stretched filaments, fibers or yarns of a vinyl halide-acrylonitrile resin, which stretched filaments, fibers or yarns previously had been stabilized against substantial shrinkage at temperatures around 120° C. by heating the same to a temperature between around 135° C. and around 175° C. for a period of between two minutes and four hours while under tension sufficient to prevent shrinkage of said filaments, fibers or yarns, and thereafter heating the thus treated article in the presence of water under superatmospheric pressure and at a tem-

perature between 105° C. and around 125° C. for a period of from thirty minutes to two hours while untensioned.

17. Process for dyeing textile articles comprising stretched dimensionally stable filaments, fibers and yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff to provide a dyeing of good color depth and excellent wash fastness and crock fastness while minimizing loss in dimensional stability of such stretched filaments, fibers and yarns, which comprises immersing for between five minutes and thirty minutes in an aqueous treating bath containing such a dyestuff and heated to between around 60° C. and 100° C., a textile article comprising stretched filaments, fibers or yarns of a vinyl halide-acrylonitrile resin, which stretched filaments, fibers or yarns previously had been modified by heating the same at a temperature between around 135° C. and around 175° C. for a period of between two minutes and four hours while under tension sufficient to prevent shrinkage of said filaments, fibers or yarns, and thereafter heating the thus treated article in the presence of the treating bath to a temperature between 105° C. and around 125° C. under superatmospheric pressure for a period of from thirty minutes to two hours while untensioned.

18. Process for dyeing textile articles comprising stretched dimensionally stable filaments, fibers and yarns of a vinyl halide-acrylonitrile copolymer resin by means of an acid-type dyestuff to provide a dyeing of good color depth and excellent wash fastness and crock fastness while minimizing loss in dimensional stability of such stretched filaments, fibers and yarns, which comprises immersing for between five minutes to thirty minutes in an aqueous treating bath containing such a dyestuff and heated to between around 60° C. and 100° C., a textile article comprising stretched filaments, fibers or yarns of a vinyl halide-acrylonitrile resin, which stretched filaments, fibers or yarns previously had been modified by heating the same at a temperature between around 135° C. and around 175° C. for a period of between two minutes and four hours while untensioned, and thereafter heating the thus treated article in the presence of humidified air to a temperature between around 125° C. and around 150° C. at atmospheric pressure for a period of from thirty minutes to two hours while untensioned.

THEOPHILUS A. FEILD, JR.
ARCHIE G. SCHOONOVER.

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Certificate of Correction

Patent No. 2,543,316

February 27, 1951

THEOPHILUS A. FEILD, JR., ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 70, for "Philoxine" read *Phloxine*; column 9, line 32, for the claim reference numeral "1" read *5*; column 11, line 51, for the word "food" read *good*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of May, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.