

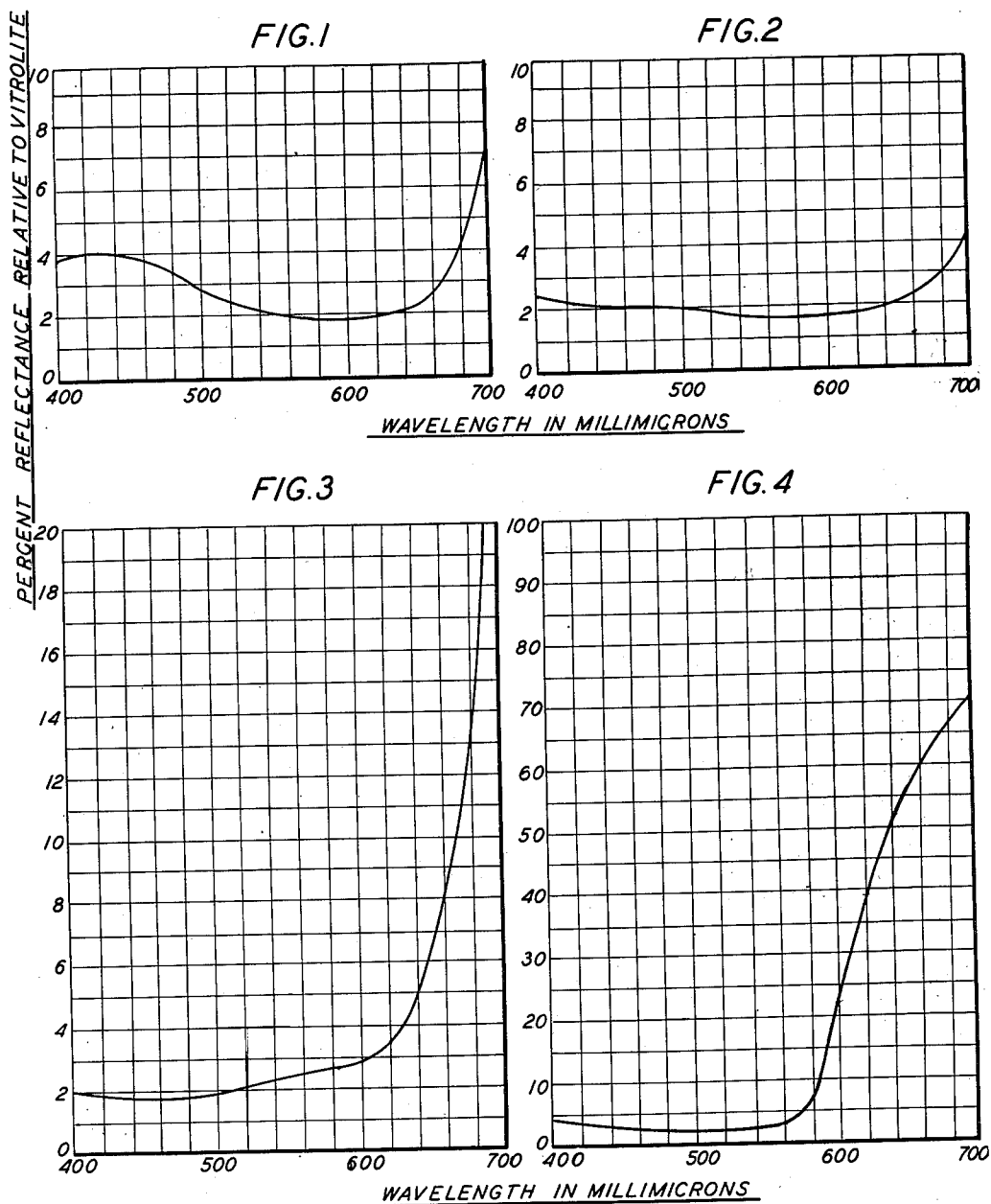
May 14, 1957

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HYDROXYLAMINE SALTS

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2 Sheets-Sheet 1



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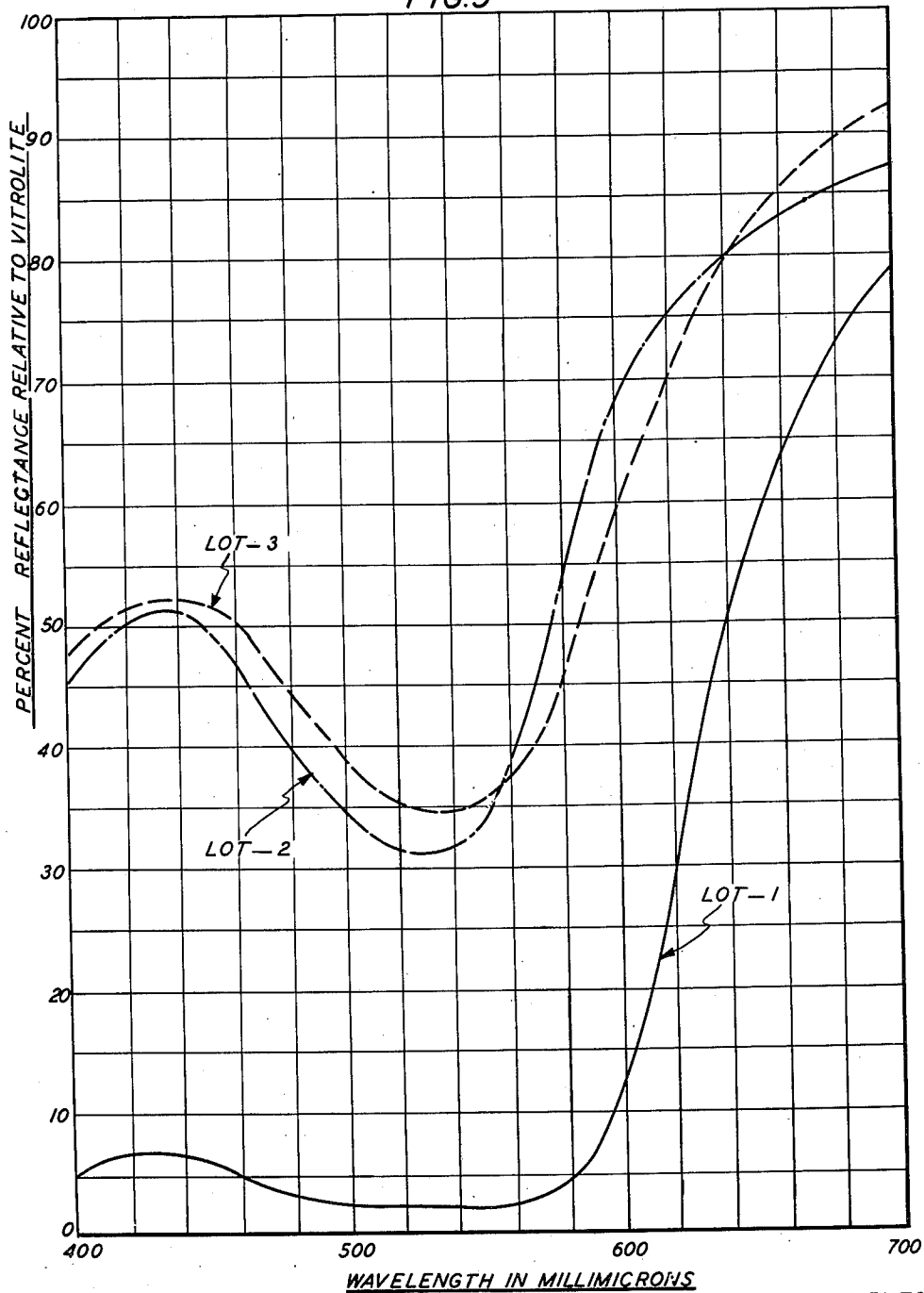
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FIG. 5



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TREATMENT OF POLYACRYLONITRILE MATERIAL WITH HYDROXYLAMINE SALTS

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15 Claims. (Cl. 8—55)

The present invention relates to the dyeing of polyacrylonitrile materials and more particularly to a process for modifying such materials so that they become capable of being dyed by conventional dyeing procedures. The invention has particular application and utility in the preparation of polyacrylonitrile textile materials for dyeing with the acid dyes so that deep level dyeings of excellent fastness are produced.

The polyacrylonitrile materials to which the present invention is applicable comprise all of those materials formed by the polymerization of acrylonitrile, alone, or in conjunction with other polymerizable substances to form copolymers, in which at least 80% of the copolymer consists of acrylonitrile in the polymerized form. Such other substances include—vinyl chloride, vinyl acetate, and other vinyl esters of mono-carboxylic acids, acrylic acid, methacrylic acid and their derivatives or homologues such as methyl methacrylate and other alkyl methacrylates, styrene and its derivatives such as α -methyl styrene and other vinyl or isopropenyl substituted aromatic hydrocarbons, methyl vinyl ketone, vinyl pyridine and its homologues, vinyl chloracetate and other vinyl esters of halo-substituted acetic acids, dimethyl fumarate, dimethyl maleate and related alkyl derivatives, vinylidene chloride, isobutylene and other polymerizable hydrocarbons. All such materials are referred to herein as "polyacrylonitrile materials or products."

The invention is of utility in the dyeing of all kinds of structures formed from such polyacrylonitrile materials, including, but not limited to, tapes, films, tubings and other molded or extruded articles. The most important application of our invention, however, is in the preparation for dyeing of textile products formed from such polyacrylonitrile materials, such as filaments and fibers, whether loose, or fabricated into the form of threads, yarns, roving, or sliver, or in the form of knitted, woven, braided or other fabric. For convenience, therefore, the invention will be further disclosed with particular reference to its application in the textile field, with the understanding that this is done for convenience and not by way of limitation of the scope of the invention.

Textile fibers formed from polyacrylonitrile materials are coming into wide acceptance both in the wool and cotton textile industries. Such fibers to be treated by this invention are prepared by conventional wet or dry spinning procedures from solutions of the polymer in suitable solvents such as NN-dimethyl formamide, NN-dimethylacetamide, tetramethylene sulfone, etc. The polymers employed for textile purposes must be of a sufficiently high molecular weight to provide good filament-forming characteristics, usually in the range 25,000 to 750,000 or higher, especially within the range 40,000 to 250,000 as determined by viscosity measurements by the Staudinger method. However, polymers having a molecular weight below or above this range may successfully be subjected to the process of this invention.

The process of this invention also can be employed in the preparation for dyeing of polyacrylonitrile copolymer materials containing less than 80% acrylonitrile. With

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textile materials of this character, however, it usually is possible to obtain adequately deep, fast and level dyeings by application of conventional practices, and, as a practical matter, acrylic copolymers containing less than 80% acrylonitrile have not proved particularly useful in the formation of textile fibers because of inherent limitations due to instability of the spinning solution, poor fiber forming characteristics, poor strength, lack of toughness and chemical inertness, inadequately high softening point, poor elastic recovery or other defects.

In contrast, the copolymers of more than 80% acrylonitrile content, particularly copolymers containing 95% to 99% acrylonitrile, produce fibers of excellent properties but, possibly by virtue of the very chemical qualities which impart these desirable characteristics, these fibers are difficult or impossible to dye by the existing dyeing methods, which difficulty has seriously limited their usefulness in the preparation of general utility fabrics. These polymeric materials are all relatively stable chemically, are insoluble in ordinary solvents and have a low water absorption, which properties make dyeing of the fibers in the conventional aqueous dye baths with the ordinary water soluble dyestuffs a difficult problem. The dyed materials, fiber or fabric, are poorly dyed initially, and generally on exposure to sunlight or upon repeated laundering have faded, stained adjacent fibers, or shown a leaching out or release of dyestuff from the fiber. With some processes foul odors are imparted to the dyed materials.

The use of carriers or assistants such as phenolic compounds, aniline, and others has been explored but without wholly satisfactory results due to undesirable effects of these materials in imparting odor to the dyed products and impairing the light fastness of the dyeing. Also, in many instances the disposal of the dye baths containing such materials presents a serious problem.

Accordingly, an object of the present invention is to improve the dyeing of polyacrylonitrile materials containing more than 80% acrylonitrile.

A further object of the invention is to provide a process for modifying such polyacrylonitrile material to render it capable of being dyed by conventional dyeing procedures.

Another object is to provide a new and valuable general purpose polyacrylonitrile textile fiber which is dye receptive in the conventional textile dyeing procedures.

Another object of the invention is to provide a process for modifying polyacrylonitrile textile material to adapt it for dyeing with acid dyes by conventional processes.

Other objects and advantages of the invention will appear as this description proceeds or will be apparent to those skilled in the art.

In the accompanying drawing Figures 1, 2, 3 and 4 are spectrophotometric curves of the dyeings of Examples 1, 2, 3 and 4 respectively. Figure 5 is a set of such curves for the dyed products of Example V.

In accordance with the invention, the polyacrylonitrile material is modified to prepare it for dyeing by treating it with an aqueous solution of hydroxylamine by heating it while wet with the solution at an alkaline pH of 7.0 to 10 or higher.

Since hydroxylamine is unavailable commercially because of its instability, we employ in practice the stable, commercially available, hydroxylamine salts such as hydroxylamine hydrochloride (available commercially as hydroxylammonium chloride) hydroxylamine sulfate (hydroxylammonium sulfate) or (hydroxylammonium acid sulfate), and include in the treating liquor an equivalent amount of an alkali for the purpose of liberating the hydroxylamine from its salts to provide free hydroxylamine for reaction with the polyacrylonitrile material. Suitable alkalis for this purpose are sodium carbonate, sodium hydroxide and other alkali metal or alkaline earth

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metal carbonates or hydroxides, quaternary ammonium hydroxides such as tetramethyl-ammonium hydroxide, tetra-ethanol-ammonium hydroxide, etc., or other organic bases such as amines or amine derivatives, e. g., ethylamine, tetra-ethanolamine, etc.

We have found that the temperature and time of treatment may be varied over wide limits while still obtaining the advantages of the invention. Conveniently the material may be treated at the boil, or at higher temperatures; temperatures of 160° F. to 225° F. give good results.

The duration of the treatment may be varied over wide limits. Treatment for from 20 to 120 minutes gives good results. There appears to be no disadvantage to longer treatment (except of course the increased cost) provided the temperature and duration are not such as to damage the material.

The pH, however, is critical and must be above 7.0. We have obtained particularly good results with pH values within the range 8.5 to 9.0.

Amounts of hydroxylamine from about 5% to about 75%, by weight on the polyacrylonitrile material have been found satisfactory when the modified material is dyed at atmospheric pressure, although the deepest dyeings were obtained in the 30% to 50% range. When the dyeing is at elevated pressure, the maximum and optimum amounts are somewhat lower, about 20% and 10% respectively.

We have found that polyacrylonitrile material, such as fiber or fabric, after modification in the hydroxylamine bath has an affinity for a wide variety of dyestuffs including full shades in acid, basic, direct, vat, acetate and sulphur colors. A full range of vivid acid dye shades may be secured and the dyeings are of good to excellent fastness to wet textile processing operations such as crabbing, fulling, scouring and also to garment cleaning operations, both laundering and dry cleaning. The dyestuffs can be applied by the procedures which are conventional in the textile industry.

The following examples of practical applications of the invention are given for purposes of illustration and not of limitation.

EXAMPLE I

A two pound tightly compressed package of polyacrylonitrile top (Du Pont Orlon, Type 41) was placed in a Morton pressure dyeing sample kettle, the temperature of the circulating water was raised to 120° F. and 8% on the weight of the top (72.5 grams) of hydroxylamine hydrochloride was added to the expansion tank in small portions over a 10 minute period. 6.6% (59.8 grams) of sodium carbonate, on the weight of the Orlon top, was dissolved in a small amount of water, cooled to room temperature and slowly added over a 10 minute interval. The pH at this time was 6.5. The temperature of the bath was raised to 200° F. over a period of 30 minutes (at which time the pH was 8.7) and maintained at 200° F. for an additional 30 minutes, at the end of which time the pH was 9.1. The bath was then dumped and the top given three rinses with cold water, each rinse consisting of filling the kettle with cold water, circulating the water for 5 minutes and then draining the kettle.

The compressed package treated as described was then dyed a navy blue in the same kettle with the following dyestuff:

3% Calcocid Alizarine Sky Blue B, C. I. 1088, Calco Chem. Div.
2.4% Anthraquinone Violet 3R, C. I. 1080, Dupont
3% Pontacyl Fast Black N2B Conc., C. I. 304, Dupont
4% conc. sulfuric acid

(Reference for dyestuff names and classification: 1952 Year Book A. A. T. C. C. and the Colour Index.) The temperature of the dye bath was raised to 200° F., the kettle closed pressure-tight and the temperature raised to 250° F. and held for one hour. The bath was then cooled

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to 200° F. and drained from the kettle. The pH of the dye bath at the end of the operation was 2.4. The dyed top was then scoured in the same kettle with ½% on the weight of the top of a long chain alcohol sulfate detergent.

A small portion of the dyed Orlon top was formed into a pad and spectrophotometrically measured for color specification (as described hereinafter) and the curve of Fig. 1 and the following colorimetric data obtained:

Description of Shade	Dominant Wave Length (Milli-microns)	Excitation Purity (percent)	Reflectance (percent)
15 Purplish Blue.....	468.0	27.6	2.2

[Color shades are described herein according to the NBS-ISCC method of designating colors (see NBS Research paper RP1239).]

Another portion of the pretreated and dyed Orlon top was braided with white Orlon top and white wool top and subjected to A. A. T. C. C. color fastness tests with the following results.

Test Method	Color fastness to—	Degree of Fastness
Standard Method 36-52 Test No. 3.	Commercial Laundering and Domestic Washing.	Class 4.
Tentative Method 25-52.	Dry Cleaning.	Class 5.
Tentative Method 5-52.	Dry and Wet Heat (Hot Pressing).	Class 4.
Standard Method 15-52.	Perspiration.	Class 5.
Tentative Method 31-52.	Pleating.	Class 5.
Standard Method 8-52.	Rubbing (Cracking).	Class 5.

Manufacturer's or Processor's Tests

Standard Method 1-52 Test No. 4.	Mill Washing and Scouring.	Class 5.
Standard Method 2-52 Test No. 3.	Fulling.	Class 5.
Standard Method 11-52 (Sulfuric Acid Method).	Carbonizing.	Class 5.
Temporary Method 55-52.	Pitting (Crabbing).	Class 5.
Temporary Method 54-52 (Test No. 2B).	Cross dyeing (Sulfuric Acid)	Class 3.

The pretreated and dyed Orlon showed no change in color or break after 30 hours of exposure at 105° F. in a type FDA-R fadeometer.

The described braid of the dyed Orlon—white Orlon—white wool was tested for fastness to decating by subjecting it to a temperature of 250° F. for 10 minutes in a conventional laboratory autoclave. There was no staining of any of the white fibers in this test and no change in shade of the braid or of the dyed Orlon.

In summary, the results of the above tests indicate that the fastness to wet processing of the dyeing of our pretreated Orlon with the selected acid color (believed to be representative of the acid colors) is much greater than the fastness to wet processing of the same color when applied to wool by the same method of dyeing.

EXAMPLE II

234 pounds of polyacrylonitrile fiber (Du Pont Orlon Type 42), in the form of tightly compressed packages of loose fiber stock, were subjected to the treatment of this invention in a Butterworth yarn dyeing kettle, which had been converted to a pressure kettle but was otherwise conventional in construction. The packages were placed in the kettle and the temperature of the circulating clean water raised to 120° F. 8% on the weight of the Orlon of hydroxylamine hydrochloride was added over a ten minute period in small portions and circulation thereafter continued for 10 minutes, then 9% on the weight of the Orlon of aqueous caustic soda (50% sodium hydroxide) was added to the expansion tank over a 20 minute interval and the temperature of the bath raised to 180° F. over a 20 minute period following addition of the last portion

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of caustic soda. Circulation was continued for 10 minutes at 180° F., the temperature raised to 190° F. and circulation continued for another 10 minute period; finally the bath was raised to 212° F. and circulated for 45 minutes. The bath then was dropped and the stock rinsed with clear cold water. The rinse water was drained off and the kettle refilled with clear cold water to which 3% of concentrated sulfuric acid was added. The temperature was raised to 160° F. and the water circulated for 15 minutes at this temperature. The bath was then drained and the stock again rinsed with clear cold water by circulating the water for 5 minutes.

The pretreated package was then dyed in the same Butterworth kettle with an aqueous dye bath containing by weight on the stock:

12.5% Pontacyl Fast Black N2B Conc., C. I. 304

0.6% Resorcin Brown 3R, C. I. 235

6.0% sulfuric acid

The temperature of the dyebath was raised to 200° F. in 15 minutes, the kettle then closed pressure-tight and the temperature raised to 250° F. over an additional 15 minutes, and then held at 250° F. with circulation of the bath for 1¼ hours. The bath then was cooled to 200° F., drained and the stock scoured with water containing ½%, on the weight of the stock, of a long chain sulfated alcohol detergent by circulating the detergent bath for 15 minutes at 160° F.

The resulting black dyed Orlon fiber stock was processed into yarn and the black yarn braided with equal parts of white Orlon and white wool yarn. This braid was then subjected to the tests described in Example I. The black dyed Orlon fiber dyed in this example showed no bleeding of color in the mill scouring, the fulling and the potting (crabbing) tests. There was no color change in the sulfuric acid carbonizing test. The dry cleaning test, the dry and wet heat (hot pressing) test and rubbing (crocking) test did not show any loosening up of the color; the undyed material in the braid was not stained. The perspiration tests showed a very light color transfer to the multi-fiber test cloth, which was evaluated as showing the dyeing to be equivalent in this respect to a chrome black on wool dyeing. The light fastness test (FDA-R, 105° F.) showed no color break after 30 hours.

A pad was made from another portion of the dyed Orlon sliver and spectrophotometrically measured, giving the curve of Fig. 2 and the following data:

Description of Shade	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
Black.....	453	8.2	1.7

Another portion of the yarn spun from the black Orlon fiber stock was woven with white wool yarn into a check pattern cut of sample cloth consisting of 60% of the black and 40% of the white fiber. The cloth was a sheen type fabric of 11.5 to 12.0 ounces per running yard 60 inches wide. This cloth was processed through conventional wet finishing operations consisting of crabbing, scouring and fulling and dry finished by the normal operations of shearing, Gessner plate pressing, and Gessner decatizing at 7 p. s. i. gauge of steam for 5 minutes. The completed finished fabric showed a clear, distinct, bright white check; there was no staining whatsoever of the white wool.

A further portion of the pretreated and black dyed Orlon fiber stock was blended with a chrome-dyed black wool stock in the proportion of 60% Orlon to 40% wool fiber, the blend spun into yarn and the yarn woven into a solid black cut of sample cloth of a sheen type weighing 11.5 to 12.0 oz. per running yard 60 inches wide. For purposes of comparison, an identical Orlon fiber stock was dyed black, with the same dyestuff employed in this

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example, by the "cuprous-ion" process under pressure at 250° F., was blended with stock from the same lot of black dyed wool in the same proportions as described above, and the resulting blend processed by the same procedures into a similar cut of sample cloth. These two sample cuts of cloth were processed by normal worsted fabric finishing routines as described above.

Comparative evaluation of the two samples by commonly used physical tests for tensile strength, abrasion resistance, pilling, crease resistance, drape, yarn slippage, tear resistance, dimensional stability, and odor showed no significant difference between the samples except as to odor. The fabric made from the Orlon fiber dyed by the "cuprous-ion" method was considered unacceptable for the garment trade because of its very noticeable and disagreeable odor. In contrast, the Orlon fabric made from the same fiber but pretreated by the process of this invention was regarded as acceptable in all respects and considered to have good characteristics for men's wear.

EXAMPLE III

228 pounds of polyacrylonitrile sliver (Du Pont Orlon consisting at least 95% of polymerized acrylonitrile), in the form of six 38 pound tightly compressed packages of top were subjected to the pretreatment of this invention and dyed a dark brown shade in the Butterworth yarn dyeing kettle of Example II. The packages were placed in the kettle and scoured with 1% on the weight of the top of a non-ionic detergent at a temperature of 160° F. for 20 minutes, then rinsed with cold water and the kettle refilled with clear water. The temperature of the circulating water was raised to 110° F. and 12% on the weight of the top of hydroxylammonium sulfate (previously dissolved in water) was added and circulation thereafter continued for 10 minutes. 9% on the weight of the top of aqueous caustic soda (50% sodium hydroxide) was added to the expansion tank of the kettle, the temperature of the bath raised to 200° F. and circulation continued for 35 minutes at 200° F. The pH at the end of this 35 minute interval was 9.6. The steam to the kettle coils was shut off and, when the temperature had dropped to 180° F., 6% (on the weight of the top) of concentrated sulfuric acid was added with continued circulation. After 20 minutes the pH of the bath was 1.6. At this point was added:

2.80% Roracyl Dark Brown B, C. I. unknown

0.70% Resorcin Brown 3R, C. I. 235

1.00% Resorcin Brown 5G 200%, C. I. 234

The temperature of the dye bath was raised to 200° F., the kettle closed pressure-tight and the temperature raised to 250° F. over a period of 20 minutes, and then held at 250° F. with circulation of the bath for 40 minutes. The pH then was 4.4. The bath was cooled to 200° F., drained and the stock scoured with clear water containing ½%, on the weight of the top, of a long chain alcohol sulfate detergent by circulating the detergent bath for 15 minutes at 160° F. The top was rinsed with clear warm water by circulating the water for 10 minutes.

A pad was made from a portion of the dyed Orlon sliver and the following spectrophotometric data and the curve of Fig. 3 obtained.

Description of Shade	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
Dusky Reddish Brown.....	494.6	77.8	2.5

All six packages of dyed fiber showed a uniform color from the center to the outside of the package and were evaluated as excellent as to color leveling.

The color fastness to wet processing was excellent and generally similar to, but somewhat better than, the

fastness of the product of Example I, being equal to that of a chrome brown dyed on wool.

The light-fastness test, using an FDA-F Fade-O-Meter at 105° F. did not show any break in color after 30 hours of exposure.

EXAMPLE IV

A two pound tightly compressed package of polyacrylonitrile fiber top, consisting at least 98% of acrylonitrile (polymerized) was placed in a Morton pressure dyeing sample kettle and scoured with ½%, on the weight of the top, of a non-ionic detergent at 160° F. for 20 minutes and then rinsed with cold water. The kettle was refilled with clear cold water, the temperature of the circulating water was raised to 120° F. and 10% on the weight of the top of hydroxylamine hydrochloride previously dissolved in warm water was added to the expansion tank in small portions over a 10 minute period. 11¼%, on the weight of the top, of aqueous sodium hydroxide (50% NaOH) was added to the expansion tank in small portions over a 20 minute interval.

The temperature of the bath was raised to 200° F., the kettle closed pressure-tight, the temperature raised to 225° F. and the bath circulated at this temperature for 30 minutes. The bath was allowed to cool, drained and the package of top given three 5 minute rinses with cold water each rinse consisting of filling the kettle with cold water, circulating the water for 5 minutes and then draining the kettle.

The package treated as described was then dyed a bright scarlet in the same kettle with the following:

6.5% Polar Red RL, C. I. 430, Geigy Co.
0.5% Resorcin Brown 5G
7.0% sulfuric acid

The temperature of the circulating dye bath was raised to 200° F., the kettle closed pressure-tight and the temperature raised to 250° F. and held for one hour. The bath was cooled to 200° F. and then drained from the kettle. The dyed top was scoured in the same kettle with ½% on the weight of the top of a long chain alcohol sulfate detergent and given one rinse with warm water.

Spectrophotometric measurement of a pad formed from a small portion of the dyed Orlon top gave the curve of Fig. 4 and the following:

Description of Shade	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
Vivid Red.....	615.2	76.7	9.7

A bright, lively scarlet shade was secured on the modified polyacrylonitrile the wet fastness of which was equivalent to that of chrome colors applied on wool. The dye was uniformly distributed from the center to the outside of the package. The results of the color fastness tests were considered very good by the standards generally accepted for worsted menswear fabrics.

EXAMPLE V

Top made from polyacrylonitrile fiber consisting essentially of acrylonitrile (polymerized) was modified by hydroxylamine treatment and acid dyed a bluish-red shade at atmospheric pressure. To compare the dye affinity of the fiber modified by the practice of this invention with the unmodified fiber, two other lots of top from the same batch, but unmodified, were dyed, one under atmospheric and the other under superatmospheric pressure, using the same dyestuff and the same concentrations of dye and acid.

Lot 1

MODIFICATION TREATMENT

A 100 gram mass of the top was immersed in a cold bath consisting of:

12% hydroxylammonium sulfate
11% liquid caustic soda (50% NaOH)

The above weights are based on the weight of the top. The material to water ratio was 1:20. The bath was brought to and maintained at the boil for 40 minutes. The modified top then was rinsed with clear warm water.

Dyeing procedure

The dyebath consisted of:

6% Pontacyl Carmine 2G, C. I. 31, E. I. du Pont de Nemours & Co.
6% sulfuric acid

The dye bath and modified top (material to water ratio 1:20) contained within an open vessel was brought to the boil in 10 minutes and the dyeing was allowed to proceed for one hour at 212° F. The modified and dyed top was thoroughly rinsed with cold water.

Lot 2

A 100 gram mass of the original unmodified polyacrylonitrile top was dyed at atmospheric pressure in exactly the same manner and with the same concentration of dye and acid as above.

Lot 3

A 100 gram mass of the original, unmodified top was dyed in a dyebath exactly the same as above but under pressure. The top was dyed in a home type 4 quart pressure cooker using a material to water ratio of 1:20. The temperature of the dyebath was raised to 200° F., the cooker closed, and the temperature further increased to 250° F. in a period of 20 minutes. The dyeing was allowed to proceed at 250° F. for one hour. The top was given one rinse with cold water after the dyeing operation.

Pads of each of the three lots of fibers were made and measured spectrophotometrically for color specification. The results are shown in Fig. 5 and below:

Lot	Description of Shade	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
No. 1—Modified Fiber Dyed at Atmospheric Pressure.	Strong Purplish Red.	493.7c	59.9	7.1
No. 2—Unmodified Fiber Dyed at Atmospheric Pressure.	Moderate Pink.	496.6c	23.2	48.9
No. 3—Unmodified Fiber Dyed at Superatmospheric Pressure.	Moderate Purplish Pink.	502.9c	18.8	44.2

The great difference in dye affinity between the modified fiber and the original fiber is illustrated by the spectrophotometric curves of Figure 5. The unmodified fiber dyed at atmospheric or super-atmospheric pressure had relatively little or no affinity for the acid dyestuff; only a very light and irregular tinting of the fiber occurred. The modified fiber dyed at atmospheric pressure, on the other hand, showed a very penetrated, uniform and substantial dyeing.

EXAMPLE VI

100 grams of top consisting of polyacrylonitrile fiber composed at least 95% of acrylonitrile (polymerized) was modified as described in Example III. The modified top was dyed with a mordant acid color from an acid bath and then after-chromed. The dyestuff used was Chrome Blue 2R (C. I. Prototype 7) which is a mordant acid

color characterized by a complete change of shade when combined with a metallic mordant. Thus, the color dyes red from an acid bath and is changed to a dark blue when after-chromed.

100 grams of the modified top was dyed in a home type 4 quart pressure cooker using a material to bath ratio of 1:20, in an aqueous dyebath containing by weight on the stock:

4% Chrome Blue 2R, Ciba Co.
6% sulfuric acid

The dyebath was brought directly to 250° F. and maintained at this temperature for one hour. The dyed top was well rinsed with warm water (105° F.). A bright medium red dyeing was secured.

The 100 grams of dyed loose top was entered into and after-chroming bath containing:

2.0% sodium bichromate
4.0% acetic acid

The after-chroming bath was raised to 250° F. and maintained at this temperature for ½ hour. 1.0% sodium bichromate and 2% sulfuric acid was added and the after-chroming continued at 250° F. for an additional ½ hour. The top then was well rinsed with cold water. A medium shade blue dyeing was secured with excellent fastness properties.

The dyed top was braided with white wool and white polyacrylonitrile top and tested for wet color fastness. The dyed top showed no bleeding, whatsoever, in the

standard crabbing, scouring and fulling tests described in Example I. There was no change in shade or color bleeding in the dry cleaning, commercial laundering, or acid or alkaline perspiration tests. The dyed top is rated an unqualified Class 5 according to the A. A. T. C. C. Yearbook for 1952 for these properties. The dyed and after-chromed top was fast to cross-dyeing with formic and with sulfuric acids. Treatment with a 5% solution of diammonium phosphate at the boil for a period of one hour did not effect any color bleeding or change of shade. This dyeing on the polyacrylonitrile top was equivalent in color fastness to the fastest chrome blue dyes applied to wool.

EXAMPLE VII

The following additional dyestuffs, representative of a wide range of types of dyes, were dyed on 100 gram lots of polyacrylonitrile top (Orlon Type 41) in the apparatus of Example VI at a material-bath ratio of 1:20, employing 4% of the dyestuff and 4% sulfuric acid (specific gravity 1.84) by weight on the fiber, at 240° F. for 1 hour.

In each instance the top was first modified in an aqueous bath of 8% hydroxylamine hydrochloride and 6.5% soda ash (by weight on the fiber) by raising the bath to 200° F. in 20 minutes, holding at 200° F. for 25 minutes, and rinsing with cold water. No wetting agents, dyeing assistants, "carriers" or swelling agents were used. After dyeing the top was washed with 1% of a synthetic non-ionic detergent at 160° F. for 15 minutes and rinsed with warm water. Spectrophotometric measurements were made with the results indicated:

Colour Index No.	Dyestuff Classification	Dyestuff	Description of Shade ¹	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
10.....	Nitro.....	Napthol Yellow S.....	Strong Greenish Yellow.....	573.0	77.7	57.6
27.....	Mono-Azo.....	Orange G.....	Strong Orange.....	587.8	86.3	42.6
31.....	do.....	Amido Napthol Red G.....	Deep Purplish Red.....	495.3c	57.7	5.6
56.....	do.....	Chromotrope 6B.....	Deep Red Purple.....	535.8c	52.3	4.6
151.....	do.....	Orange II.....	Vivid reddish orange.....	596.2	89.7	21.7
176.....	do.....	Fast Red A.....	Vivid Red.....	630.0	68.6	7.1
234.....	Primary Dis-Azo.....	Resorcin Brown.....	Strong reddish orange.....	595.9	82.5	14.1
235.....	do.....	Resorcin Dark Brown.....	Strong reddish Brown.....	603.0	62.8	7.1
252.....	Secondary Dis-Azo.....	Brilliant Crocein M.....	Vivid Red.....	624.5	60.0	15.4
288.....	do.....	Sulphon Cyanine G.....	Purplish Black.....	461.0	13.4	2.1
304.....	do.....	Nerol 2B.....	Black.....	400.0	9.3	2.1
430.....	Dis-Azo Colors from Diamines.....	Polar Red.....	Strong Purplish Red.....	595.9c	64.8	5.8
487.....	do.....	Acid Anthracene Red 3B.....	Vivid Red.....	620.5	73.5	9.3
640.....	Pyrazolone.....	Tartrazine.....	Vivid Yellow.....	578.4	81.8	53.6
642.....	do.....	Polar Yellow.....	Strong Yellow.....	578.7	84.8	38.1
1053.....	Anthraquinone.....	Alizarin Saphirol SE.....	Strong Blue.....	477.6	53.2	12.0
1078.....	do.....	Alizarin Cyanine Green.....	Moderate Blue Green.....	490.5	34.8	8.0
1080.....	do.....	Anthraquinone Violet.....	Moderate Purple.....	548.3c	48.1	6.5
1088.....	do.....	Alizarin Sky Blue B.....	Strong Purplish Blue.....	471.7	64.0	3.8
667.....	Diamino-Derivatives of Triphenylmethane.....	Brilliant Milling Green B.....	Lt. Bluish Green.....	486.7	53.4	7.8
698.....	Triamino-Derivatives of Triphenylmethane.....	Formyl Violet S4B.....	Strong bluish purple.....	438.0	62.0	3.7
712.....	Amino - Hydroxy - Derivatives of triphenylmethane.....	Patent Blue V.....	Brilliant Blue Green.....	487.4	38.8	25.2
735.....	Derivatives of Diphenylnaphthylmethane.....	Naphthalin Green V.....	Brilliant Bluish Green.....	495.1	32.7	19.6
<i>Xanthene Colors</i>						
758.....	Amino-Derivatives of Xanthene Fluorene Colors—Rhodamine.....	Violamine R.....	Strong reddish purple.....	543.0c	49.8	7.7
768.....	Amino-Derivative of Xanthene Fluorene Colors — Hydroxy - Phthaleins.....	Eosine G.....	Brilliant Red.....	619.5	40.5	25.6
801.....	Quinoline.....	Quinoline Yellow.....	Strong Yellow.....	576.0	85.2	58.8
<i>Azine Colors</i>						
833.....	Aposfranines-Rosindulines.....	Wool Fast Blue.....	Moderate purplish blue.....	469.6	55.0	4.1

See footnotes at end of table, columns 11 and 12.

UNCLASSIFIED COLORS

Colour Index No.	Dyestuff Classification	Dyestuff	Description of Shade ¹	Dominant Wave Length (milli-microns)	Excitation Purity (percent)	Reflectance (percent)
None	Acid	Roracyl Dark Brown B	Weak Brown	600.0	12.2	5.7
	Acid (Du Pont)	Roracyl Dark Green B	Weak Blue Green	490.2	16.0	2.5
	Acid (Sandoz)	Xylene Milling Green B	Strong Blue Green	496.3	18.7	40.4
	Acid (Du Pont)	Milling Red SWB (125%)	Vivid Red	627.8	65.2	11.2
	Acid (Geigy)	Irgalan Grey BL	Weak Purplish Blue	473.8	19.9	7.6
	Metallized Acid Dye	Calcofast Wool Bordeaux RB conc.	Moderate Pink	494.5c	13.8	40.8
	do.	Calcofast Wool Yellow N	Light Yellow	576.6	33.8	75.8

COMBINATION DYEINGS

833		3% Wool Fast Blue BLA ex.	Dusky Bluish Purple			
1080		2% Anthraquinone Violet 3R				
307		1.5% Pontacyl Fast Black BBN		465.8	40.5	2.3
1088		3% Calcocid Alizarin Blue Sky	Dusky Purplish Blue			
1080		2% Anthraquinone Violet 3R				
307		0.3% Pontacyl Fast Black BBN		471.2	30.2	2.4
None		2.5% Roracyl Dark Brown B				
234 pr ²		0.5% Resorcin Brown 3R				
234		1.0% Resorcin Brown 5G (200%)	Weak Brown	589.5	31.7	4.9
319	Direct	Pontamine Fast Blue 2RL	Dusky purplish blue	468.5	30.0	2.2
Pr ² 71	do.	Pontamine Fast Blue SFL	Purplish Black	467.0	15.7	2.0
Pr 425	do.	Chlorantine Fast Green BLL	Dusky Green	499.8	11.2	8.5
Pr 428	do.	Chlorantine Fast Red 6BLL	Deep Purplish Red	645.0	50.7	4.6
Pr 246	do.	Solantine Red 8BLN	Vivid Red	623.1	69.8	8.3
Pr 277	do.	Fastusol Red Violet LRL	Dark Purplish Red	500.4c	45.2	6.3
None	do.	Pontamine Fast Orange 2GL	Strong reddish orange	596.4	83.0	15.8
Pr 379	do.	Fastusol Gray LVGL	Dark Bluish Gray	472.0	4.5	5.5
None	do.	Pontamine Yellow LRA	Moderate Yellowish Orange	585.2	68.0	41.1

¹ Shades are described according to the NBS-ISCC method of designating colors (see NBS Research Paper 1239).

² Pr indicates similar to or a foreign prototype.

With the above "Direct" cotton dyestuffs the amount of sulfuric acid was increased to 6%.

The spectrophotometric data given in the foregoing examples were obtained by use of a General Electric Company Recording Photoelectric Spectrophotometer with a G. A. F.-Librascope Automatic Tristimulus Integrator, using a white Vitrolite glass reference standard and calculated for C. I. E. Illuminant C, each figure being the average of measurements on the face and back of the pad. The calibration of the instrument was done in the usual manner with a didymium filter, Corning 5120 and the Vitrolite glass working standard. The calibration of these glasses may be referred to in National Bureau of Standards Test No. 106956 of December 12, 1945.

The compressed packages treated in the examples were formed from polyacrylonitrile sliver by the method described in the patent applications of Robert C. Wilkie, Serial No. 208,562, filed January 30, 1951, now Patent No. 2,707,806, and Serial No. 359,602, filed June 4, 1953. These packages have been compressed to a size less than $\frac{2}{3}$ the volume of the uncompressed sliver and are so dense and tightly compressed as to be unyielding to the touch and to retain substantially permanently their shape and size. Notwithstanding the high density and tightness of these packages, the dyeings of the examples were very level and uniform from the inside to the outside of the packages.

We have observed that the fiber modified by our process is yellow in color and insoluble in the usual solvents for acrylonitrile polymers and copolymers, such as dimethylformamide, dimethylsulfoxide, tetramethylurea, and succinonitrile. The physical and mechanical properties of the fiber evidently are not adversely affected by the treatment and valuable, commercially effective and economical dyeing is made possible.

As is illustrated in the foregoing examples, the wet fastness properties of molecularly dispersed acid dyestuffs applied to polyacrylonitrile fibers modified by our process approach in excellence those of the aggregated, or colloidal, acid colors on wool.

The wet fastness of the colloidal acid dyes applied to our modified polyacrylonitrile fiber equals even that

of many of the chrome dyes applied to wool. In general, we have found that any acid dye that may be used successfully in wool dyeing has an affinity for the acrylonitrile polymers modified by our pretreatment.

We have been able successfully to employ, with our modified polyacrylonitrile material, the mordant acid or chrome dyes in the same general manner that they are used to color wool and to secure a wide range of shades of good color depth. Thus, we have applied the chrome dyestuffs to the modified acrylonitrile polymer by the well known bottom chrome (chrome mordant) process, the after-chrome (top-chrome) process, and by the meta-chrome (monochrome, or chromate) process.

As is known, the true alizarine dyestuffs (true mordant dyestuffs), as distinguished from the mordant acid colors which may be dyed with or without a mordant, will not dye without a mordant. We have found that polyacrylonitrile fiber modified by the process of the invention can be successfully bottom-chromed with sodium bichromate, and then dyed with these true mordant colors in an acid bath.

We have also found that the modified polyacrylonitrile fiber has a good dye receptivity for the "direct cotton" colors when dyed from an acid bath in the manner conventional in the application of those dyes to wool. The direct cotton dyes listed in Example VII showed very good affinity for the modified polyacrylonitrile fiber, the bath exhaustion of dyestuff was very good and in some cases complete. The fiber was uniformly and substantially dyed.

Other ingredients in the dyebath, the nature of the dyestuff, and the conditions of dyeing may be varied to a considerable degree and the effects of these changes readily determined by one familiar with the chemistry and mechanics of dyeing. Commercial dyeing techniques using ratios of material dyed to water of from 1:4 to 1:30 may be successfully employed.

The dyeing processes may involve the dyeing of loose fiber, filament, top, yarn, thread, fabric, etc. in conventional or specialized dyeing equipment utilizing atmospheric or super-atmospheric pressures.

The invention is also applicable to the printing of

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color, for example, as is done in the cotton print goods industry. One skilled in the printing art will be able to select the formulation to be used, conforming to the basic concepts of this invention, to produce the results and satisfy the requirements of the particular fabric and equipment. For example, an alkaline solution of a hydroxylamine salt and a conventional gum thickener may be printed on the fabric and the printed fabric steamed to effect local modification of the polyacrylonitrile polymer. The fabric could then be piece dyed to produce selective coloration of the printed pattern.

Similarly, one skilled in the practices of continuous dyeing may select the equipment and procedure to be used, and, using the principles of this invention, produce solid shade dyed fabrics. For example, the fabric may be padded with an alkaline solution of a hydroxylamine salt and fiber modification completed by steaming, heating with infra-red equipment, or running the fabric through a molten metal bath, or through a series of boxes containing hot water. The modified fabric having the dye affinity can then successfully be continuously dyed by methods and processes well known in the art.

We claim:

1. The process for treating a polyacrylonitrile product to improve its dyeing characteristics which comprises wetting the product with an aqueous solution in which is included a salt of hydroxylamine and an alkali in an amount sufficient to adjust the pH of the solution to between 7.0 and 10.0 and heating the product while wet with said solution in the presence of hydroxylamine produced in said solution by the action of the alkali on the hydroxylamine salt.

2. The process of claim 1 in which the solution is heated to a temperature above 160° F.

3. The process of claim 1 in which the solution is heated to a temperature between 160° F. and 225° F.

4. The product of the process of claim 1.

5. The process for treating a polyacrylonitrile product to improve its dyeing characteristics which comprises wetting the product with an aqueous solution in which is included 5% to 50% of a salt of hydroxylamine, by weight on the polyacrylonitrile, and an alkali in an amount sufficient to adjust the pH of the solution to between 7.0 and 10.0 and heating the product while wet with said solution, at a temperature between 160° F. and 225° F. for from 20 to 120 minutes in the presence of hydroxylamine produced in said solution by the action of the alkali

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on the hydroxylamine salt, and rinsing the product with water.

6. The process of claim 5 in which the salt of hydroxylamine is hydroxylamine hydrochloride.

7. The process of claim 5 in which the salt of hydroxylamine is hydroxylamine sulfate.

8. The product of the process of claim 5.

9. The process for treating a polyacrylonitrile textile material to improve its dyeing characteristics which comprises wetting the material with an aqueous solution in which is included 5% to 50% of a salt of hydroxylamine, by weight on the polyacrylonitrile, and an alkali in an amount sufficient to adjust the pH of the solution to between 7.0 and 10.0, heating the solution to a temperature between 160° F. and 225° F. for from 20 to 120 minutes, and rinsing the material with water.

10. The process of claim 9 in which the salt of hydroxylamine is hydroxylamine hydrochloride.

11. The process of claim 9 in which the salt of hydroxylamine is hydroxylamine sulfate.

12. The process for dyeing a polyacrylonitrile product which comprises heating the product while wet with an aqueous solution in which is included 5% to 50% of a salt of hydroxylamine, by weight on the polyacrylonitrile, and an alkali in an amount sufficient to adjust the pH of the solution to between 7.0 and 10.0, and thereafter dyeing the product.

13. The product of the process of claim 12.

14. The process of claim 12 in which the dyeing is with an acid dye at a pH below 7.0.

15. A process for acid dyeing a polyacrylonitrile textile material which comprises heating the material in an aqueous bath free of acid dyestuff and in which is included 5% to 50% of a salt of hydroxylamine, by weight on the material, at a pH between 7.5 and 10.0 and a temperature above 160° F. for from 20 to 120 minutes, thereafter immersing the product in a bath at a pH below 7.0, the bath containing an acid dyestuff, and heating the article in the bath.

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