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DYEING CONTINUOUS FILAMENT NYLON WITH 1:1 PREMETALLIZED DYES AND MIXTURES THEREOF WITH DYE ASSISTANTS

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U.S. Cl. 8—26 13 Claims

ABSTRACT OF THE DISCLOSURE

Improved process for level, lightfast dyeing of polyamide fibers and textile articles comprised thereof by contacting same with an aqueous dye bath containing specific 1:1 premetallized dyes (I, II and III), dyeing assistant and, preferably, metal complexing agent.

This invention concerns a process for level, lightfast dyeing of polyamide fibers, especially in the form of carpets and automobile upholstery fabrics, with specific 1:1 premetallized dyes, dye assistants and, for optimum results, metal complexing agents.

BACKGROUND

Recent years have seen the development of articles such as carpets and automobile upholstery fabrics made from nylon and other polyamide fibers develop into a large volume business. Many problems have arisen in achieving dyeings satisfactory from economical, technical and aesthetic viewpoints. Of the various kinds of dyes available, disperse dyes have been largely used for dyeing such articles, particularly full width nylon carpets where problems with streakiness are liable to occur. Level dyeings may be achieved in this manner, but lightfastness is generally not adequate, and they are often deficient in chemical fastness and brightness of shade. In addition, disperse dyes are among the most expensive types of dyes. Acid dyes, while usually superior to disperse dyes in brightness and fastness, have the drawback of giving streaky, uneven dyeings. This problem is discussed at length by Schmutzler in "Textil Praxis" International Edition, vol. 19, No. III, pages 119–123 (1964). Therein it is pointed out that the results of dyeing with 1:1 metal complex and 1:2 metal complex dyes are characterized by "heavy marking of irregularities in the yarn."

Surprisingly the process of this invention enables the use of specific 1:1 metal complex dyes of superlative lightfastness with resulting streak-free, even dyeings. The particular adjuvants used, and application according to the method prescribed, give uniquely satisfactory dyeing performance in the required qualities of fastness to light, levelness, and freedom from streaks. These qualities are particularly important in such applications as the economical piece dyeing of full width nylon carpeting, and in dyeing fabrics for automobile upholstery.

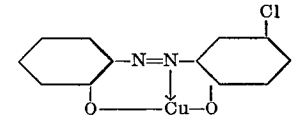
It is an object of this invention to provide a process for level, streak-free dyeing of polyamide fibers, particularly in nylon automobile upholstery fabrics and in full width carpets of bulked, continuous filament polyamide fibers. It is a further objective to provide a process for dyeings of superior lightfastness on polyamide fibers.

BRIEF SUMMARY OF THE INVENTION

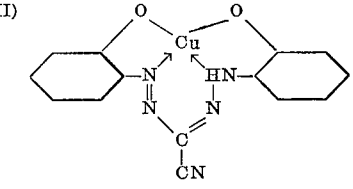
These and other objectives are accomplished, in the dyeing of polyamide fibers (and articles comprised thereof) including the steps of contacting said fibers with an aqueous dye bath, following by rinsing and drying; by the improved process which comprises contacting said fibers with an aqueous bath containing 1:1 premetallized dyes, I,

II and III (listed below), alone or in combination; a dyeing assistant selected from dodecylbenzenesulfonic acid diethanolammonium salt or disodium dodecyldiphenylether disulfonate; and, optionally, a metal complexing agent selected from sodium citrate, sodium fluoride or a mixture of the tetrasodium salt of ethylenediamine tetraacetic acid and anhydrous copper sulfate. Dyes I, II and III have the structure:

(Red Dye-I)

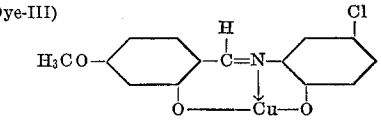


(Blue Dye-II)



and

(Yellow Dye-III)



DETAILED DESCRIPTION OF INVENTION

Many efforts have been made to perfect processes for dyeing textile articles comprised of polyamide fibers especially a process for piece dyeing of carpets made from bulked continuous filament nylon. This type of nylon made possible the production of attractive and durable carpets at popular prices. Unfortunately, efforts to piece dye these carpets with acid or premetallized dyes most often resulted in streaks. Streak-free dyeings could be made with disperse dyes, but as above mentioned these dyes suffered from shortcomings in chemical fastness, lightfastness, and brightness of shade, especially when compared with some acid and premetallized dyes. Premetallized dyes in general exhibit a high degree of lightfastness, a quality of prime importance in the dyeing of carpets.

It has now been found that textile articles comprised of polyamide fibers, especially nylon carpets, may be dyed effectively with dyes I, II and III above in conjunction with specific dyeing assistants. These assistants are disodium dodecyldiphenylether disulfonate and dodecylbenzenesulfonic acid diethanolammonium salt.

By polyamide is included those synthetic linear polycarbonamides characterized by recurring amide linkages as an integral part of the main polymer chain such as poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(m-xylene adipamide), poly(p-xylylene sebacamide), polycaprolactam and the like as well as copolyamides. Textile articles comprised of polyamide fibers include automobile upholstery fabrics, carpeting, articles intended for outdoor uses and the like. The preferred polyamide is poly(hexamethylene adipamide) and the most advantageous application of the instant process is in dyeing full width carpets comprised of trilobal, jet-bulked nylon yarn.

The red (I), blue (II) and yellow (III) 1:1 premetallized dyes employed in the instant process may be prepared as follows:

The red dye, I, is prepared by diazotization of o-aminophenol and coupling to p-chlorophenol. The isolated dye is heated with a water soluble cupric salt in aqueous dimethylformamide. The copper complex is isolated by further dilution with water and subsequent filtration.

The blue dye, II, is prepared by diazotizing o-aminophenol (2 mols) and coupling to cyanoacetic acid (1 mol), with simultaneous decarboxylation. The product is metallized by heating with a water soluble cupric salt in aqueous pyridine and isolated in the same manner as the red dye I.

The yellow dye, III, is prepared by condensing 4-methoxysalicyladehyde with 2 - amino - 4 - chlorophenol, followed by treatment with copper salt and pyridine.

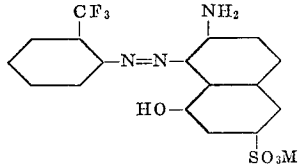
In adition to dimethylformamide and pyridine, the copper complexing may be carried out in aqueous solutions of pyridine, alpha or beta picoline or mixtures of isomeric picolines and other similar basic materials.

By "1:1 premetallized" is meant a ratio of one metal molecule to one dye (or organic) molecule.

The amount of dye(s) used will vary according to the depth of shade desired. A range of from about 0.2 to 2.0% by weight, based on the textile article weight, is normally sufficient to give any desired shade depth.

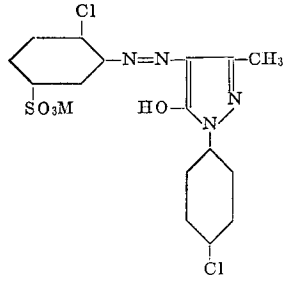
The red, yellow and blue dyes of this invention may be blended to provide a full line of attractive shades on polyamide articles. Testing has proven their superiority to other dyes of similar type in the required qualities of levelness, lightfastness and streak-freeness, particularly in dyeing nylon carpets in full width or rope form.

Further variations in shade may be attained by applying one or more of the dyes of the invention with selected acid dyes having superior qualities as regards levelness, lightfastness, streakfreeness and fastness to fumes. Among the acid dyes suitable for coapplication are red monazo acid dyes of the formula



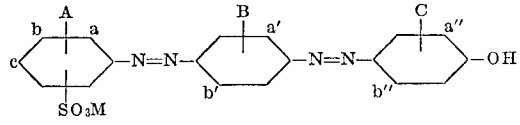
(M=H, ammonium radical or alkali metal)

as more fully described in U.S. patent application Ser. No. 876,032, filed Nov. 12, 1969; yellow monazo acid dyes of the formula



(M=H, ammonium radical or alkali metal)

as more fully described in U.S. patent application Ser. No. 634,110, filed Apr. 27, 1967; and disazo yellow orange dyes of the formula



(M=H, ammonium radical or alkali metal)

as more fully described in U.S. Pat. No. 3,485,814, filed Dec. 17, 1965; all three in the name of S. B. Speck. In such coapplication, the total amount of above-described 1:1 premetallized dyes and acid dyes used is preferably in the range of from about 0.02 to 2.0% by weight, based on article weight. The dyes of the invention may also be used in conjunction with disperse dyes of adequate quality to meet specific shade requirements.

The dyeing assistant is dodecylbenzenesulfonic acid diethanolammonium salt or disodium dodecyldiphenylether disulfonate. It is believed to function by masking some of the amine end groups in the polyamide molecule, thereby promoting an even take-up of the dye. The dyes are assumed to be attached to the nylon through these amine end groups. When carpets are made of bulked, continuous filament nylon, the supply of filament used may exhibit variation in the number of available amine end groups. This may be due to slight differences in chemical processing or in some cases to physical differences. In any case, the dyeing of such carpets with acid dyes or any dyes which are presumed to react with the available amine end groups will exhibit differences corresponding to the variation in filament quality. The usual result is a streaky dyeing, wherein the nylon filament possessing a high number of amine end groups will be dyed a deeper shade than a filament having a lower number of amine end groups. The function of the dyeing assistant is to effectively minimize these differences resulting in a uniform dyeing without streaks. The optimum proportion of the dyeing assistant is about 0.5 to 4.0 percent by weight, based on article weight, 1.5% being the amount used in most tests. Streak coverage and levelness are improved with even higher proportions of assistant, up to 2½% or 3%, but as quantities above 4% are used, exhaust becomes poorer, dye is wasted and economic advantage is lost.

Dyeings are preferably carried out at or near the boil (about 95°–100° C.) in order to achieve satisfactory level dyeing across the entire width of the carpet (or fabric) in the shortest time, and to make the most economical use of the dye. Lower dyeing temperature results in slow transfer of the dyes throughout the carpet width, causing heavy dyeing of the portion of the carpet near the point of dye addition and light dyeing of the part of the carpet remote from that point. This phenomenon is most appreciated in commercial application, where carpet widths in the order of 12 ft. may be dyed, while it is more difficult to discern in laboratory dyeings. Higher temperature (above 100° C.) promotes decomposition of the dyes and may result in off shade dyeings. Another effect of low temperature (below 95° C.) is unsatisfactory exhaust, which means that the available dye is not completely taken up by the article being dyed. Temperatures of 95° C. to 100° C. offer the best combination of results as regards dyebath exhaust, levelness of dyeing and economy of time and material.

The article is contacted by (preferably immersed in) said aqueous dye bath for from about 1 to 4 hours. While 1 to 2 hours give satisfactory dyeings, optimum leveling is achieved after 2 to 3 hours of dyeing time. Dyeing time of less than 1 hour results in unsatisfactory leveling. At least one hour is required for accomplishing uniform shade from side to center of full width carpets. Also 1 hour is the minimum time required for satisfactory exhaust of the dye from the dye bath. When dyeings are prolonged beyond 4 hours, there are indications of shade change.

The most satisfactory pH range for the process of this invention is 6 to 7.5. When dyeings are carried out at lower pH, dyebath exhaust becomes increasingly poorer. The same is true at higher pH. This is believed due to an optimum solubility of the dye in the fiber at the preferred pH, the dye being more soluble in water at lower and higher pH. The pH is controlled by conventional methods, as e.g., by adding either disodium phosphate or acetic acid as required as shown in Example 1 below.

In carrying out the instant process it has been found that, while the use of tap water causes dye degradation in 2 hours or less, dyeing can be carried out for about 3½ hours in distilled or deionized water without evidence of dye degradation. Still further, when sodium citrate, sodium fluoride or a mixture of the tetrasodium salt of ethylenediamine tetraacetic acid and anhydrous copper sulfate is present in the dyebath as a metal complexing agent, dyeings can be carried on for at least about 6 hours at the boil without appreciable degradation of dye. The optimum required amount of these agents is proportional to the amount of dissolved heavy metal in the water used. Practically speaking (based on article weight), 1% to 5%

sodium citrate; 1% to 4% sodium fluoride; or 50 parts per million to 250 parts per million of the tetrasodium salt of ethylene diamine tetraacetic acid along with 50 to 250 parts per million of anhydrous copper sulfate in the dyebath are satisfactory for most of the water commercially available. Larger amounts of metal complexing agents may be used but offer no advantage. The weight proportion of water (to textile article) in the bath may generally be varied from about 20:1 to 50:1 without deleterious effect. Following dyeing, the carpet is rinsed and dried according to conventional techniques.

The resulting process offers many advantages long desired in dyeing nylon carpets. Technically the dyeings are extremely lightfast and are streak-free. Full width dyeings of carpets are even, and chemical fastness and other desirable qualities are satisfactory. The colors are attractive and can be blended to produce shades most desired in the trade. Economically, advantages are attained in several ways. The ability to dye by piece dyeing methods eliminates the necessity for large stocks of colored yarns which formerly had to be maintained by dyers who wished to use dyes of superior properties. Only a limited stock of the required dyes is necessary. The dyes and adjuvants are not high-priced relative to other usable classes of dyes. Because of the unusual lightfastness of these dyes, carpets dyed by the process of this invention can be used in applications hitherto not open to nylon carpetings. Applications in automobile carpets and upholstery and even outdoor uses in direct sunlight may be attained.

As used hereinabove and in the following examples, the term "levelness" refers to the degree of uniformity of shade depth from side to center to side of a relatively wide piece of material such as a carpet. "Shade" indicates both color and the depth or lightness and darkness of such color. If a dye lot is found to be "off-shade" (e.g. it is found to be reddish-blue when it should be greenish-blue), it may be "shaded" with a different dye to bring it "on shade." A one color carpet should have a uniform shade; it is not acceptable to have the sides shaded a darker color than the center.

"Lightfastness" indicates the stability or colorfastness of the dyed article to light. The lightfastness test in the following examples was performed according to the American Association of Textile Chemists and Colorists procedure entitled "Colored Fastness to Light," Tentative Test Method 16E–1964, using a Xenon Lamp for 80 hours (or more). Lightfastness was evaluated according to the following scale:

Rating	Indicates	Explanation
5	No break	Negligible or no change.
4	Slight break	Slightly changed.
3	Moderate break	Noticeably changed.
2	Poor break	Considerably changed.
1	Severe break	Severely changed.

A rating of 4 to 5 is usually regarded as acceptable fastness to light.

The following examples describe the invention in further detail. These examples are intended to be merely illustrative of the invention and not in limitation thereof. All parts are by weight unless otherwise indicated.

EXAMPLES

Example 1.—Standard procedure for dyeing bulked, continuous filament nylon carpet

The carpet used is backed with polypropylene or jute. It is comprised of 3700-denier 204-continuous filament, trilobal, jet-bulked yarn, melt-spun from poly(hexamethylene adipamide) flake. The yarn may be conveniently jet-bulked with a jet such as taught by Hallden et al. in U.S. Pat. 3,005,251. The carpet is first scoured in a bath containing 40 parts of water (based on carpet weight as 1), 0.01 part of a molar adduct of 20 moles of ethylene oxide and technical oleyl alcohol and .02 part commercial (26%) ammonium hydroxide. The scour is started at 43° C. and the temperature raised at 2° C. per minute to 82° C. and held there for 20 minutes. The bath is drained and the carpet rinsed well with clear water.

Dyeings then carried out by adding to the vessel 40 parts of water at 27° C., .03 part of sodium citrate, and the temperature raised to 43° C. at 2° C. per minute. Next are added .02 part of monosodium phosphate and .018 part of dodecylbenzene sulfonic acid diethanolammonium salt, plus .002 part of the yellow dye (III), .001 part of the red dye (I) and .0005 part of the blue dye (II). The temperature is raised to boiling (99°–100° C.) at the rate of 2° C. per minute. The pH is maintained throughout at 6.5 to 7.5 by adding either disodium phosphate or acetic acid as required Dyeing is continued for 2 hours at the boil until side to center levelness is reached. The bath is then dropped and the carpet is rinsed with clear water for 10 minutes. The rinse is repeated twice more and the carpet finally dried.

The dyeing assistant disodium dodecyldiphenolether disulfonate may be substituted for the dodecylbenzene sulfonic acid diethanolammonium salt with substantially equally good results.

An attractive beige shade is achieved by the above combination of dyes with satisfactory levelness and excellent lightfastness.

Example 2.—Effect of dyeing time

A dyeing was performed as in Example 1. Samples were removed at intervals and compared for stability and levelness (side to center shading) with the previous sample.

TABLE I

Hours at boiling temperature	Side to center shading			Stability
	Left	Center	Right	
0	15% strong	Control	15% strong	
.5	do	do	do	
1.0	10% strong	do	do	5–4 B.
2.0	5% strong	do	10% strong	5–4 B.
3.0	Level			4 W.
4.0	do			5–4 R.
5.0	do			5–4 D.
6.0	do			5–4 R and W.

In this dyeing the carpet was 25 yards long by 32½ inches wide. Samples were cut out of the carpet at the stated intervals, rinsed and dried before comparing them. The system of grading used under the above heading "stability" is shown below:

Lightfastness key	Shade change
5—no break	W—weaker
4—slight break	M—monotone
3—moderate	R—redder
2—poor break	Y—yellower
1—severe break	B—bright
	D—duller

It is seen from the above data that about 3 hours was an optimum time for dyeing in this example. Optimum leveling was achieved after 2 to 3 hours of drying time. Dyeing times longer than 3 hours showed no advantage and evidence of minor shade change was seen at the 6 hour point.

Example 3—Effect of dyeing assistant

Dyeings were performed according to the procedure of Example 1 except that varying amounts of dodecylbenzenesulfonic acid diethanolammonium salt dyeing assistant were used for each example. In the table below the amount of red, blue and yellow color in the beige dyed samples was determined instrumentally by reflec-

tance measurement. Minimum reflectance corresponds to maximum amount of color on the sample.

TABLE 2

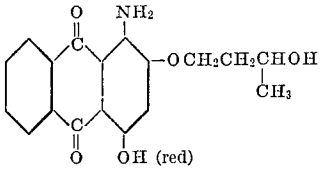
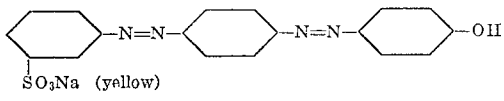
Dye assistant, percent	Yellow, percent reflectance	Red, percent reflectance	Blue, percent reflectance
.30	16.0	24.0	37.5
.60	15.5	23.0	34.5
.9	15.5	23.0	33.5
1.2	14.5	21.5	31.0
1.8	15.0	22.0	31.5
2.4	15.5	22.5	31.5
3.0	16.0	23.0	32.0

It is evident from these data that maximum utilization of dye is attained with concentration and the dyeing assistant at approximately 1.0%. On the other hand levelling as determined by visual inspection of the samples, was not satisfactory until 1.8% of the dyeing assistant was present and further improvement could be seen in the 2.4% and 3.0% samples. Thus it appears that 1.8% to 3.0% is the optimum amount of dodecylbenzenesulfonic acid diethanolammonium salt to be used to give the best combination of levelling and dye utilization.

Example 4.—Lightfastness of different types of dyes

In the table below a comparison of lightfastness and levelness is shown for beige shade dyeings made using three groups of dyes, first of all the dyes and process of this invention, secondly disperse dyes of the best quality, and thirdly acid dyes of the best quality without the dyeing assistant. The key for grading the samples is the same as shown in Ex. 2.

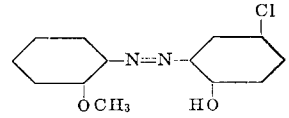
TABLE 3

Dyes		Lightfastness, zenon arc std., hours to a "4" break	Levelness
Red Dye I Blue Dye II Yellow Dye III	Beige	350	Very good.
Disp. Dye C.I. 11,855 (yellow) Disp. Dye:  OH (red)	do	100	Do.
Disp. Dye C.I. 62,500 (blue)			
Acid Dye:  (yellow)	do	150	Very poor, unacceptable.
Acid Dye C.I. Acid Red 266 Acid Dye C.I. Blue 58			

It is clear that the dyes and process of our invention give dyeings of superlative lightfastness, at the same time producing levelness essentially equal to that attained by disperse dyes.

Example 5.—Synthesis of red dye I

Ortho-anisidine (30.8 grams), was added to 125 ml. of water and 50 ml. of concentrated hydrochloric acid and stirred to complete solution. Ice (125 grams), was added and the solution cooled to below 5° C. 50 ml. of 5 normal sodium nitrite solution was added in small portions as it reacted until an excess remained for 20 minutes. The excess nitrite was then destroyed with sulfamic acid. The resulting diazo solution was coupled at 10° C. to a solution containing 39.0 g. parachlorophenol, 25 ml. of 30% sodium hydroxide solution, 400 ml. of water and 25 g. of sodium carbonate. After all of the diazo solution had been added, tests showed an excess of parachlorophenol and no diazo group present. The solution was stirred for 16 hours (overnight), then filtered, washed with hot water and dried in a vacuum oven at 70° C. A dry weight of 65 g. of product was obtained. It had the structure:



Metalization was accomplished as follows: about 24.9 g. of the above dye was added to 125 ml. DMF which contained 25 g. of sodium acetate anhydrous. The reaction mixture was heated to 90° C. and 25 g. of finely powdered cupric chloride were added fairly rapidly. The mixture was then heated to 95° C. to 99° C. and held there for three to four hours.

The heating was then discontinued and, to isolate the metalized dye, 250 ml. water were gradually added and the stirring continued for another hour.

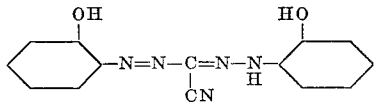
The solid was filtered off and washed until free of DMF (dimethylformamide).

The wet filter cake was milled with sand in the presence of a sulfonated naphthalene formaldehyde condensate to a particle size of 1 to 5 microns. The sand was removed by filtration and the paste was spray dried to yield a disperse powder which was standardized to 40% active ingredient, using sugar or other commonly used materials as diluent.

Example 6.—Synthesis of blue dye II

Ortho-aminophenol (150 grams), was added to 700 ml. of water and the slurry stirred for 15 minutes, then 260 ml. of concentrated hydrochloric acid was added and the resulting solution stirred for 30 minutes. About 700 g. of ice was added and the solution thus cooled to 0° to 5° C. Sodium nitrite (275 ml. of 5 N solution) was next added as rapidly as possible with good agitation, keeping the temperature below 5° C. The solution was stirred at 0° to 5° C. for an additional hour and the excess nitrite destroyed with sulfamic acid. The resulting diazo solution was filtered and added at 0° to 5° C. over a period of 45 minutes to a solution prepared by mixing 60 g. of cyanoacetic acid and 500 ml. of water, to which 250 ml. of 30% sodium hydroxide was added. While adding the diazo solution, the pH was held at 12±1 by adding small amounts of 30% sodium hydroxide as necessary. At completion a positive test for presence of excess coupler was evidenced. The solution was stirred for 2 hours, then filtered and washed with 1500 ml. of water. After

drying in a vacuum oven at 80° C., 204 g. of dry product was recovered, structure was:



Metallization was accomplished as follows: about 68 g. of the above product was dissolved in 250 ml. of pyridine, and 70 g. of copper sulfate pentahydrate in 100 ml. of water containing 10 ml. of pyridine was added after the reaction mixture had been heated to 50° C.

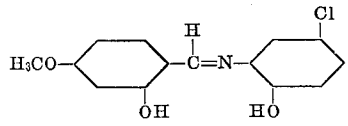
The mixture was then heated to 90–95° C. and held there for three to four hours.

The heating was then discontinued and the reaction mixture allowed to cool to room temperature with agitation. When this temperature was reached 750 ml. of water were slowly added and the slurry stirred for another hour.

The solid was then filtered off and washed pyridine free with water. Milling and standardization were carried out as in Example 5.

Example 7.—Synthesis of yellow dye III

A solution of 63 g. of 4-methoxy-2-hydroxybenzaldehyde in 325 ml. of ethanol was prepared and to it was added a solution of 59.6 g. of 2-amino-4-chlorophenol in 80 ml. of ethanol dropwise over a period of 20 minutes. The mixture was heated to the boil under a reflux condenser for 1 hour, then allowed to stir and cool to room temperature overnight (16 hours). The solid material was filtered off and bottled. The yield of alcohol-wet material was 175 g. This product had the structure:



The above wet cake was dissolved in 450 ml. of pyridine and heated to 60° C. A solution was prepared of 140 g. of copper-sulfate pentahydrate in 200 ml. of water and added dropwise over a period of ½ hour to the pyridine solution. The mixture was held at 60° C. for an additional 1 hour, then cooled over 1 hour to 30° C. Then 500 ml. of water was added and the slurry cooled to −20° C. and filtered. The solid was washed first with 250 ml. of 30% pyridine in water solution and lastly with 800 ml. of distilled water. The product was milled as in Ex. 5.

EXAMPLE 8

A comparison was made between the recommended adjuvants of the instant process and the dyeing assistant of U.S. Pat. No. 3,278,253 which shows dyeings on textile materials having a basis of a synthetic linear polyamide with complex metal dyestuffs. Dyeings to a beige shade were carried out as in Ex. 1 except for the changes in additives as noted.

Thus, it is seen that U.S. Pat. 3,270,253's leveling agent for use with metal complex dyestuffs is quite unsatisfactory for use with the metal complex dyes of this invention as it fails to maintain satisfactory dye stability, in contrast to the dyeing assistant dodecylbenzenesulfonic acid diethanolammonium salt, and also does not give satisfactorily streak-free dyeings.

Example 9.—Self color dyeing with blue dye II

Dyeing was carried out according to the procedure of Example I using .005 part of blue dye II and .03 part of dyeing assistant. The following data were obtained: Lightfastness key is shown in Example 2.

TABLE V

Dyeing assistant	Hours exposure to xenon arc-(FadeOmeter)	Lightfastness compared to std.(unexposed)
Disodium dodecyldiphenyl ether disulfonate	80	5
Do	240	5–4
Dodecylbenzenesulfonic acid Diethanolammonium salt	80	5
Diethanolammonium salt	240	5–4

Example 10.—Self color dyeing with red dye I

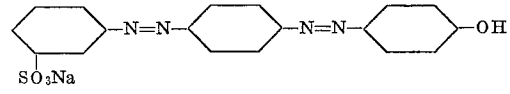
Dyeings were carried out as in Example 1 using .005 part of red dye I and .03 part of dyeing assistant. The following data were obtained. Lightfastness key is shown in Example 2.

TABLE VI

Dyeing assistant	Hours exposure to xenon arc-(FadeOmeter)	Lightfastness compared to std.(unexposed)
Disodium dodecyldiphenyl ether disulfonate	80	5
Do	240	5–4
Dodecylbenzenesulfonic acid Diethanolammonium salt	80	5
Diethanolammonium salt	240	5–4

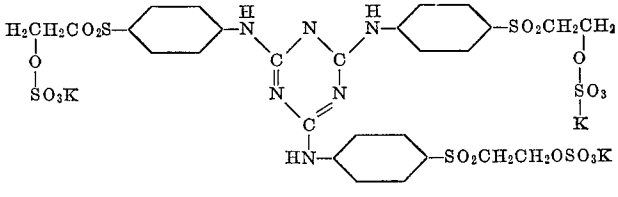
Example 11.—Dyeing with coapplication of yellow acid dye

A dyeing was made according to the general procedure of Example 1, using .00187 part of red dye (I), .00385 part of blue dye (II) and .00935 part of the yellow acid dye



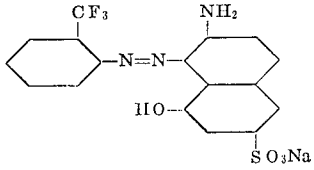
The dye bath pH was held near 6.0 during this dyeing. Satisfactory levelness was attained after one hour of dyeing. A satisfactory green shade was achieved with a lightfastness rating of 5–4 W after 280 hours exposure to the Xenon Lamp.

TABLE IV

Additive	Streakfreeness	Dye test sampled after— 4 hrs.	5 hrs.	6 hrs.
Dodecylbenzenesulfonic acid diethanolammonium salt plus sod. citrate	Excellent	5-4R	5-4R	5-4R and W.
	Poor	5-4R	5-4R	3-2R.
Above plus sodium citrate	do	5-4R	4-3R	2-1R.

Example 12.—Dyeing with coapplication of yellow and red acid dyes

A dyeing was made according to the general dyeing procedure of Example 1, using .00368 part of blue dye (II), .0106 part of the yellow acid dye used in Example 11 and .000152 part of the red acid dye



A satisfactory green shade similar to that achieved in Example 11 resulted. Levelness was satisfactory after 1 hour dyeing. The lightfastness rating was 5–4 W after 280 hours exposure to the Xenon Lamp.

Example 13.—Procedure for dyeing polyamide upholstery fabric

An upholstery fabric is knit of conventional polyamide yarns of 70-denier, 34-filaments to the threads, the filaments being of round cross-section. The fabric piece is first scoured in the same manner as used in Example 1 for the polyamide carpet.

To the dyeing vessel is added, based on polyamide textile material, 40 parts of water, .015 part of disodium dodecyldiphenylether disulfonate, .02 part of ammonium acetate (or enough to adjust pH to 6.0), and the dye. The temperature is raised to boiling at the rate of 2° C. per minute and the bath boiled for 5 minutes. The bath is held at the boil for an additional 45 minutes and dropped. The material is thoroughly rinsed in clear water, removed and dried.

Three solid color dyeings (a, b, and c) were so made, using in each case:

(a) .0025 part of red dye (I);
(b) .0025 part of blue dye (II); and
(c) .0025 part of yellow dye (III).

A fourth dyeing, to beige shade, was so made using .0027 part of yellow dye (III), .00105 part of red dye (I) and .0006 part of blue dye (II).

All four of the above dyeings were streak-free and showed satisfactory levelness.

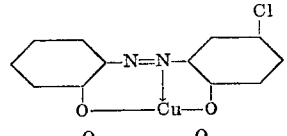
As seen above, the subject invention provides an improved process for level, streak-free, lightfast dyeing of polyamide textile articles.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for obvious modifications will occur to those skilled in the art.

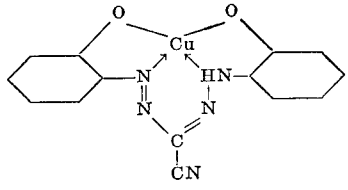
What is claimed is:

1. In a process for dyeing textile articles comprised of continuous filament nylon, comprising the steps of contacting said article with an aqueous bath, rinsing and drying said article; the improvement which comprises contacting said article with an aqueous bath containing 1:1 premetallized dyes selected from the group consisting of

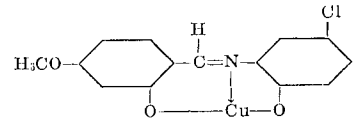
(I)



(II)



(III)



and mixtures thereof; and from 0.4 to 4.0% by weight based on the textile article of a dye assistant selected from the group consisting of dodecylbenzenesulfonic acid diethanolammonium salt and disodium dodecyldiphenylether disulfonate.

2. Claim 1 wherein said article is automobile upholstery fabric.

3. Claim 1 wherein said article is nylon carpeting.

4. Claim 1 wherein said dye bath further contains a metal complexing agent selected from the group consisting of sodium citrate, sodium fluoride and a mixture of the tetra sodium salt of ethylenediaminetetraacetic acid and anhydrous copper sulfate.

5. Claim 4 wherein said article is contacted for a period of from about 1 to 4 hours and the bath is maintained at a pH of from about 6 to 7.5 and at a temperature of from about 95° to 100° C.

6. Claim 5 wherein said dye bath contains, based on article weight, from about 0.02 to 2.0% of said dyes and from about 0.5 to 4.0% of said dye assistant.

7. Claim 6 wherein said dye assistant is dodecylbenzenesulfonic acid diethanolammonium salt.

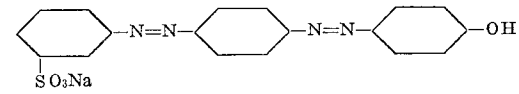
8. Claim 7 wherein said metal complexing agent is from about 1 to 5%, based on article weight, of sodium citrate.

9. Claim 8 wherein said article is nylon carpeting.

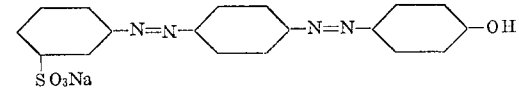
10. Claim 8 wherein said article is nylon upholstery fabric.

11. Claim 1 wherein said dye bath further contains one to three acid dyes.

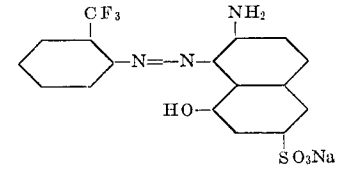
12. Claim 11 wherein said premetallized dyes are dyes (I) and (II) and wherein said acid dye is the yellow acid dye



13. Claim 11 wherein said premetallized dye is dye (II) and wherein said acid dyes are the yellow acid dye



and the red acid dye



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P. C. IVES, Assistant Examiner

U.S. Cl. X.R.

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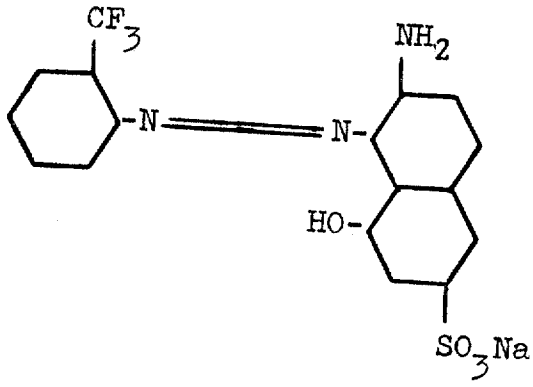
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,592,584 Dated 7/13/71

Inventor(s) William J. Link and Hermann W. Pohland

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 12, Claim 13, the final structural formula should read



Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents