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DYEING OF POLYACRYLONITRILE FIBERS

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This invention relates to the dyeing of synthetic hydrophobic filaments and staples, including yarns and fabrics made therefrom. More particularly, this invention relates to the dyeing of polyacrylonitrile filaments and staples, including yarns and fabrics made therefrom.

As is well known, within recent years a large variety of synthetic filaments and staples as well as yarns and fabrics made therefrom have appeared on the market. Invariably, the satisfactory dyeing of each one of these materials has posed problems over and above those encountered in the dyeing of natural materials of vegetable or animal origin such as cotton, linen, wool and silk. In fact, in many instances, it has been necessary to develop a new line of dyes for use in the dyeing of some types of synthetic materials.

Comparatively recently, a new synthetic material consisting of highly orientated continuous filaments of polyacrylonitrile has been introduced commercially under the trademark Orlon. Continuous filament Orlon, as well as yarns and fabrics made therefrom, has a high dry and wet strength, a high resistance to stretching and a high flex life. In addition, Orlon dries rapidly and exhibits outstanding resistance to attack by bacteria and fungi. Because of these and many other favorable characteristics of Orlon there is no doubt that this synthetic material will come into increasingly wide use in the immediate future. However, continuous filament Orlon, as well as yarns and fabrics made therefrom is highly hydrophobic and is very difficult to dye. When an attempt is made to apply presently available dyes by conventional dyeing methods to continuous filament Orlon, including yarns and fabrics made therefrom, color adsorption by the Orlon is usually zero to very slight. Also contemplated for future commercial production is Orlon staple, and yarns and fabrics made therefrom, is less difficult to dye than continuous filament Orlon and yarns and fabrics made therefrom but nevertheless presents many difficult problems to the dyer.

A number of methods have been suggested for increasing the color take up of Orlon in the dyeing thereof. These include the use of assistants in the dye bath such as aniline, the cresols, anthranilic acid, resorcinol, phloroglucinol, cyclohexanol, et cetera. These assistants have an appreciable positive effect with some dyes (but not by any means with all dyes) but many of these assistants are obnoxious to use in the dye house, are difficult to remove from the dyed material and some of them are very expensive.

It has also been found that deeper dyeings are obtained, especially when employing acetate dyes, by conducting the dyeing at two or three atmospheres pressure and a dye bath temperature corresponding thereto. Also, a similar effect is obtained by padding with an excess of dye (at atmospheric pressure) and then steaming the filament, yarn or fabric at one to two atmospheres or by drying and subjecting to dry heat at temperatures of 420–450° F. Unfortunately, many acetate dyes sublime when subjected to pressure steaming and/or dry heating.

Furthermore, many dyehouses do not have equipment suitable for pressure dyeing or the pressure steaming or dry heating of padded filaments, yarns or fabrics.

The difficulty of dyeing continuous filament Orlon fabric with presently available dyes employing conventional dyeing methods (including certain modifications thereof) is shown by the following more specific discussion.

The dyeings of continuous filament Orlon fabric were all performed under basically constant conditions. The fabric swatch was prepared for dyeing by boiling off for a short period in 1% Duponol solution. (Duponol is a registered trademark of a synthetic surfactant.) The boiled off fabric was rinsed and added to the dye bath, the weight ratio dry fabric:dye bath being 1:160. The dry fabric:dye weight ratio was 10:1. The dye bath also contained 1% Duponol as a leveling agent. The dyeing was conducted at the boiling point for a period of two hours.

Orlon was first dyed with Cellanthrene Brilliant Blue FFS (a typical acetate dye) at a series of pH values. Dyeings at pH 7 and 9 were less even and less deep than at pH 3 and 5 although the difference was not great and in all instances the take up of dye was very low and was very uneven. On the basis of these results, care was exercised to maintain a slightly acid bath in all future dyeings. The use of resorcinol or phloroglucinol (20 g./l. dye bath) as an assistant resulted in slightly improved dye adsorption at the lower pH values. With resorcinol especially a considerable improvement in the levelness of the dyeing was obtained.

An attempt was made to improve the dyeing with Cellanthrene Brilliant Blue FFS through use of ethanol or dioxane as primary assistants. The presence of even 2% ethanol in the dye bath resulted in a considerable decrease in the take up of dye by the fabric and with 50% ethanol present no dye was apparently adsorbed although undoubtedly a trace was taken up as the fabric was snow white, having lost entirely the characteristic ecru or cream color of Orlon as commercially produced. This effect is undoubtedly due to an optical bleach brought about by the take up of a trace of the blue dye. With 2% dioxane in the dye bath there was no significant change in dye adsorption, with 10% present there was an appreciable decrease and at 50% dioxane no dye was taken up and the Orlon had the usual ecru or cream color of Orlon as commercially produced. (Obviously, when these primary assistants are present in the dye bath, especially when present in large amounts, the boiling point is lower than when the only liquid present is water. Escape of these primary assistants as well as of water during the dyeing operation did not occur since all dyeings described herein were run under reflux.)

Dyeings with Eastman Blue BNN exhibit a generally similar pattern to that described in the preceding two paragraphs. Adsorption of dye was slight and the levelness of dyeing left much to be desired. Phloroglucinol and even more especially resorcinol resulted in more even dyeings and a slightly deeper shade. The use of ethanol or dioxane as primary assistants gave exactly the same results as described with respect to Cellanthrene Blue FFS; again with 50% ethanol present a perfect optical bleach was obtained.

Celliton Black BA is taken up by continuous filament Orlon fabric to give a teal color. The use of phloroglucinol as an assistant results in a bluer and of resorcinol in a greener and deeper shade than obtained in the absence of these assistants. The use of ethanol or dioxane as primary assistants gives results generally similar to those described in connection with the two blue dyes previously considered. With 50% ethanol the optical bleaching effect was again observed but a few threads in the

3 fabric exhibited a barely perceptible take up of color. With 50% dioxane, the fabric had a very faint overall bluish cast.

Eastone Red B, Eastone Red R, Eastone Rubrine C and Eastone Rubrine R all dye continuous filament Orlon fabric a pale and very uneven pink. In the presence of 20 g. per liter resorcinol in the dye bath, the pink color is largely lost and the fabric is colored a pale pinkish-brown. Eastone Violet BGF hardly colors Orlon and the color adsorption is very uneven, Eastone Blue BGF gives a very pale and very uneven blue. In the presence of resorcinol, Eastone Violet BGF is not adsorbed and Eastone Blue BGF gives a very light gray.

Eastone Yellow 6GN, Eastone Yellow 5G, Eastone Yellow GN conc., Eastone Fast Yellow GLF, Eastone Yellow RN and Eastone Fast Yellow 4RLF all give pale yellow shades on filament Orlon fiber. On using resorcinol as an assistant, very slightly to slightly deeper shades are obtained with the first three dyes mentioned; with the remaining three dyes resorcinol has no effect.

Eastone Brown 2R colors continuous filament Orlon fabric a very pale and uneven orange; in the presence of resorcinol the color is gray. Eastone Orange 3R gives a pale and uneven orange which becomes brownish when resorcinol is present in the dye bath as an assistant. Eastone Scarlet BG colors continuous filament Orlon fabric a pale and uneven pink; in the presence of resorcinol an old rose results somewhat deeper and less uneven than the color obtained in the absence of the assistant.

Finally, a developed acetate dye (Eastman Black SN) was examined. Obviously, the application of this particular dye necessitated a considerable departure from the previously described basic procedure. This material was applied to the fabric, was diazotized with an excess of nitrous acid and coupled with an excess of phloroglucinol. While this procedure gives a jet black on acetate, on continuous filament Orlon fabric a pale yellow buff was obtained. The use of ethanol or dioxane as primary assistants was decidedly deleterious. Ethanol at low concentrations (2% and 10% in the dye bath) resulted in pale, dirty and uneven colors; at 50%, no color was adsorbed. Low concentrations of dioxane gave dirty and uneven browns and at 50% the dye adsorption was decidedly less than in the absence of dioxane.

The above observations demonstrate that the satisfactory dyeing of continuous filament Orlon is extremely difficult. A large group of conventional acetate dyes (acetates, like Orlon, are hydrophobic) give, at best, pale shades and, more frequently than not, very uneven dyeings. The use of resorcinol or phloroglucinol as assistants results in some improvement in a few instances but usually these materials have either no effect or a deleterious action. Such primary assistants as ethanol and dioxane have, at best, no action at low concentrations and greatly inhibit or entirely prevent dye adsorption at high concentrations. Due to the many highly desirable properties of Orlon there is no doubt that this synthetic material will come into increasingly wide use in the immediate future and accordingly dyes that can be applied satisfactorily to Orlon would be of great utility and value.

One object of my invention is to provide a class of dyes having a high affinity for synthetic hydrophobic filaments and staples as well as yarns and fabrics made therefrom.

Another object of my invention is to provide a class of dyes having a high affinity for polyacrylonitrile filaments and staples as well as yarns and fabrics made therefrom.

A further object of my invention is to provide an improved method for the dyeing of synthetic hydrophobic filaments and staples, including yarns and fabrics made therefrom.

An additional object of my invention is to provide an

improved method for the dyeing of polyacrylonitrile filaments and staples, including yarns and fabrics made therefrom.

Other objects of my invention will become apparent as the description thereof proceeds.

I have discovered that a certain narrow and circumscribed class of monoazo dyes exhibit a comparatively high affinity for continuous filament Orlon including yarns and fabrics made therefrom. As is well known, monoazo dyes are prepared by the reaction (coupling) of a diazotized amine with a suitable coupling component, usually an amine or phenol. I have discovered that if the amine to be diazotized lacks substituents of certain types and if the coupling component carries certain types of substituents in certain configurations a monoazo dye is produced having a high affinity for Orlon.

In preparing monoazo dyes exhibiting a satisfactory affinity for Orlon, I have discovered that the amine to be diazotized must carry no substituents of a highly hydrophilic nature. The coupling component is an amine or phenol possessing at least one substituent that is not highly hydrophilic in a position meta to the amino or phenolic group.

Among amines which, when diazotized and coupled with materials conforming to the above criteria, give dyes exhibiting a high affinity for Orlon may be mentioned aniline, p-chloroaniline, p-anisidine, p-nitroaniline, m-aminophenol, m-anisidine, o-anisidine, 4,6-dinitro 2-aminotoluene, 4,6-dinitro 2-aminophenol (picramic acid) and beta (2-amino 4,6-dinitrophenyl) ethanol.

Among materials which, when coupled with diazotized amines conforming to the above criterion, give dyes exhibiting a high affinity for Orlon may be mentioned m-cresol, m-toluidine, resorcinol, m-phenylenediamine, phloroglucinol (1,3,5-trihydroxy benzene), phloramine (3,5-dihydroxyaniline), 3,5-diaminophenol, 1,3,5-triamino benzene and 2,4,6-triamino toluene.

If the amine diazotized carries a strongly hydrophilic group as a substituent, the resulting diazo compound when reacted with a coupling component conforming to the above criteria, produces a dye having little or no affinity for Orlon. Among such amines may be mentioned 2-aminophenol 4-sulfonic acid, 4-chloro 2-amino phenol 6-sulfonic acid, 4-nitro 2-aminophenol 6-sulfonic acid and 1-amino 2-naphthol 4-sulfonic acid. Similarly, if an amine with no strongly hydrophilic groups is diazotized and coupled with an amine or phenol carrying a hydrophilic group and/or lacking a non-hydrophilic group positioned meta to the amino or hydroxyl group, again dyes are obtained having little or no affinity for Orlon.

Continuous filament Orlon fabric was dyed with materials prepared in accordance with the teachings of my invention following the basic dyeing procedure previously given.

In most instances, the colors of filament Orlon fabric dyed with a number of dyestuffs prepared in accordance with the teachings of my invention are described below on the basis of the Royal Horticultural Society Colour Chart (RHS). In this color chart, the complete spectrum range is divided, in equal gradations, into 64 full hues numbered in spectral sequence from 1 (Sulfur Yellow) through the oranges, reds, blues, greens and finally back to yellow again at 64 (Dresden Yellow).

Each full hue may also appear as a lighter tint of the full hue, indicated by the prefix 6, 5 or 4 added to the full hue designation and separated therefrom by a dash (—). Taking, for example, full hue 7, its relative tint is designated 6—7, its relatively lighter tint 5—7 and its relative still lighter tint 4—7.

In addition, the full hues and tints may be grayed, this being indicated by prefixing one or more zeros to the designation in question. Thus, 06—7 refers to the relative tint of full hue 7 once grayed, 005—7 the relatively lighter tint of full hue 7 twice grayed, et cetera.

Finally, any of the above designations may carry a

suffix, separated from the designation proper by a virgule (/). When no suffix appears, the full hue (or the above described modifications thereof) is referred to while suffixes 1, 2, and 3 are graduated strengths of the full hue (or modifications thereof), suffix 3 designating the weakest of these graduated strengths.

For a variety of reasons it is impossible in many instances to make an absolutely exact match between a dyed fabric and an individual color of the color chart. For one thing, the publication of the chart has not been completed as yet so frequently an exact match of a given sample is not to be found in presently available sections of the chart and occasionally even a reasonably close approximation is missing. Furthermore, the difference in luster and surface texture between dyed Orlon fabric and the color chips of the chart makes exact matches rather difficult to achieve. In spite of these and other difficulties, in most instances this system permits the colors of the dyed fabrics to be expressed in definite terms which enable those interested to obtain an exact or nearly exact reproduction of the color by consulting the color chart.

The following compilation describes some 30 representative dyes made in accordance with the teachings of my invention and gives the color of continuous filament Orlon fabric when dyed with these dyes, usually in accordance with the previously described color chart. In this compilation, the amine diazotized is first given followed by the intermediate or intermediates with which the diazotized amine is coupled to give the dye or dyes.

Aniline:

Phloroglucinol. Red dye produced. On Orlon, RHS Carrot Red, 6—12

p-Chloroaniline:

Resorcinol. On Orlon, RHS Chinese Yellow, 6—6/1

Phloroglucinol. Red dye produced. On Orlon, RHS Yellow Ochre, 0—7/2

Phloramine. On Orlon, RHS Egyptian Buff, 4—7

1,3,5-triaminobenzene. On Orlon, RHS Yellow Ocher, 0—7/3

m-Aminophenol:

Resorcinol. On Orlon, RHS Yellow Ocher, 0—7/2

Phloroglucinol. Black dye produced. On Orlon, RHS Majolica Yellow, 0—9/3

Phloramine. On Orlon, RHS Yellow Ocher, 0—7/3

3,5-diaminophenol. On Orlon, golden brown.

1,3,5-triaminobenzene. On Orlon, light brown.

o-Anisidine:

Phloroglucinol. Dark red dye produced. On Orlon, RHS Yellow Ocher, 0—7/2

m-Anisidine:

Phloroglucinol. Reddish orange dye formed. On Orlon, RHS, Yellow Ocher, 0—7/2. (Very slightly deeper shade than o-anisidine-phloroglucinol dyeing, above.)

p-Anisidine:

Resorcinol. Brownish gold on Orlon. Phloroglucinol. Purple red dye produced. On Orlon, RHS Egyptian Buff, 4—7/1

1,3,5-triaminobenzene. On Orlon, oxidized during application.

p-Nitroaniline:

m-Cresol. On Orlon, RHS Chinese Yellow, 6—6

m-Toluidine. On Orlon, RHS Mars Orange, 0—13/3

Resorcinol. On Orlon, RHS Maize Yellow, 6—7

Phloroglucinol. Dark purple dye formed. On Orlon, RHS Yellow Ochre, 0—7/1

Phloramine. On Orlon, RHS Majolica Yellow, 0—9/1

1,3,5-triaminobenzene. On Orlon, RHS Egyptian Buff, 4—7/2

4,6-dinitro 2-aminotoluene:

m-Phenylenediamine. On Orlon, RHS Spanish Orange, 0—10/2

Phloroglucinol. On Orlon, RHS Chrome Yellow, 6—5/2

Picramic acid:

Resorcinol

Phloroglucinol

Phloramine

1,3,5-triaminobenzene. On Orlon, dyes produced by reacting diazotized picramic acid with the above coupling components gave various shades of old rose. Couplings with phloramine and with resorcinol gave comparatively gray shades while those with phloroglucinol and the triaminobenzene gave relatively lighter and brighter shades.

Beta (2-amino 4,6-dinitrophenyl) ethanol:

Resorcinol. On Orlon, brownish buff.

Phloroglucinol. On Orlon, very light buff.

Phloramine. On Orlon, RHS Yellow Ocher, 0—7/3.

3,5-diaminophenol. On Orlon, RHS Nasturtium Orange, 6—10/2.

1,3,5-triaminobenzene. On Orlon, RHS Apricot Orange, 6—9/1.

The use of resorcinol (20 g./l.) as an assistant gave quite variable results. This assistant resulted in slightly deeper shades when used with aniline-phloroglucinol, p-chloro aniline-phloroglucinol, p-nitroaniline-m-cresol, p-nitroaniline-resorcinol, 4,6-dinitro 2 - aminotoluene-phloroglucinol, picramic acid-resorcinol, picramic acid-1,3,5-triaminobenzene, beta (2-amino 4,6-dinitrophenyl) ethanol-phloroglucinol and beta (2-amino 4,6-dinitrophenyl) ethanol-1,3,5-triaminobenzene dyes. Use of the assistant gave appreciably deeper shades with m-aminophenol - phloroglucinol and o-anisidine-phloroglucinol dyes and considerably deeper shades with p-chloroaniline-phloramine and p - nitroaniline-1,3,5-triaminobenzene dyes.

Use of resorcinol as an assistant gave slightly lighter shades with p-nitroaniline-phloroglucinol, picramic acid-resorcinol and picramic acid-phloramine dyes and considerably lighter shades with m-aminophenol-resorcinol, m-aminophenol-3,5-diaminophenol and beta (2-amino 4,6-dinitrophenyl) ethanol-resorcinol dyes.

Resorcinol as an assistant gave rise to a considerably yellower and brighter dyeing with the p-anisidine-resorcinol dye, a very much darker dyeing with the p-nitroaniline-m-toluidine coupling and a duller and browner shade when employing the p-nitro aniline phloramine dye. With other dyes of the above compilation, the use of resorcinol as an assistant had no visible effect on the dyeings obtained.

Be it remembered, that while my invention has been described by means of numerous examples thereof, these are illustrative and non-limiting and it is to be understood that my invention covers all changes and modifications of the examples thereof, herein chosen for purposes of disclosure, that do not constitute departures from the spirit and scope of my invention.

I claim:

1. The method of dyeing a material selected from the group consisting of Orlon filaments, staples, yarns and fabrics comprising treating the Orlon in an aqueous dye bath containing a monoazo dye formed by coupling a diazotized amine selected from the group consisting of aniline, anisidine and picramic acid with a material selected from the group consisting of resorcinol and phloroglucinol.

2. The method of dyeing a material selected from the group consisting of Orlon filaments, staples, yarns and fabrics comprising treating the Orlon in an aqueous dye bath containing a monoazo dye formed by coupling diazotized aniline with a material selected from the group consisting of resorcinol and phloroglucinol.

3. The method of dyeing a material selected from the group consisting of Orlon filaments, staples, yarns and fabrics comprising treating the Orlon in an aqueous dye bath containing a monoazo dye formed by coupling a

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diazotized anisidine with a material selected from the group consisting of resorcinol and phloroglucinol.

4. The method of dyeing a material selected from the group consisting of Orlon filaments, staples, yarns and fabrics comprising treating the Orlon in an aqueous dye bath containing a monoazo dye formed by coupling diazotized picramic acid with a material selected from the group consisting of resorcinol and phloroglucinol.

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