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RESERVING AGENT FOR ACRYLONITRILE POLYMER BASE FIBERS

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A valuable and significant contribution to the synthetic fiber art has been the development and provision of the "nitrile alloy" class of fibers. Such man-made fibers are comprised essentially of an acrylonitrile polymer base which contains in the polymer molecule at least about 80 percent by weight of acrylonitrile, advantageously polyacrylonitrile, which has been proficuously modified without sacrifice of or compromise in its basic fiber properties by alloying the acrylonitrile polymer base, as it were, with beneficial additaments or constituents that are adapted to achieve one or more ameliorative ends for the fiber product. Primarily, and of exceptional benefit, the "nitrile alloy" fibers contain appropriate functional components that render the fiber product remarkably and permanently receptive of many of a wide variety of dyestuffs. Because of this, "nitrile alloy" fibers are readily dyeable to deep and level shades of lasting coloration by practice of ordinary dyeing techniques and procedures using the usual materials for the purpose. By their superior attributes in these as well as other particulars, the "nitrile alloy" fibers are clearly and easily distinguishable from the conventional prototype acrylonitrile polymer fibers, including the usual and well known copolymeric varieties, with which the art is familiar and which are oftentimes referred to and known as being "acrylic" fibers.

Predominantly desirable and advantageous members of the "nitrile alloy" class of synthetic fibers and the like are those, hereinafter more fully delineated, that are comprised of acrylonitrile polymer substrates and which contain minor integrant proportions of either, or both, various N-vinyl lactam polymers and copolymers or derivatives thereof; N-vinyl-2-oxazolidinone polymers and copolymers or derivatives thereof; or various N-vinyl-3-morpholinone polymers and copolymers or derivatives thereof.

As paradoxical as it may seem, there are instances wherein the exceptional and capacious receptivity to dyestuffs of "nitrile alloy" fibers might advantageously be restrained or partially or completely diminished in order that such characteristic of the fiber product might be basically altered so as to provide it with a partial or complete degree of resistance to becoming stained or colored with dyestuffs.

For example, if a stain-free, white fiber product is desired from a "nitrile alloy" material, such as a cloth or fabric article, it would be advantageous for the "nitrile alloy" to be provided in such a form as to be capable of complete resistance to becoming stained or colored by dyes or other color-imparting substances with which the "nitrile alloy" may come in contact.

Of at least commensurate practical significance is the problem of producing white or two-tone effects on "nitrile alloy" fibers when they are dyed in the presence of other fibers, such as cellulose fibers or wool and other proteinous fibers (both natural and artificial or synthetic in origin) with which the "nitrile alloy" fibers may be blended as well as that of achieving union dyeing or uniform color

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level in such fibers of "nitrile alloy" fibers that are being dyed with certain dyestuffs so that union-dyeable blends might be provided. As is widely appreciated in the art, union-dyeable blends are those that are comprised of diverse fiber constituents which are capable of being dyed in the same dyeing treatment, or series of treatments, to the same or substantially the same uniform and balanced degree of coloration of each of the fibers in the blend. For purposes of achieving the immediately above mentioned ends, it would be advantageous, as is apparent, for "nitrile alloy" fibers to be provided in such a form that they would have only a partial resistance to or reserving action against dyestuffs and coloring agents, depending on whether diverse or equal tones of coloration are desired in the dyed blend in which it is contained.

It would be especially beneficial if a reserving or dye-resisting agent for "nitrile alloy" fibers were particularly effective on practically all of the several major classes of dyestuffs, including, in particular, vat and soluble vat dyes in addition to direct, acid, acid premetallized and the other varieties of dyestuffs ordinarily utilized for use in the coloring of "nitrile alloy" products. This would be highly desirable since certain of the reserving agents that are effective for many dyestuffs on "nitrile alloy" fibers are frequently not especially effective in restraining the use of vat or soluble vat dyestuffs on such synthetic fibers. This is the case, for example, with the various polyphenolic polymer reserving agents that have been disclosed by the present inventors with others in the concurrently filed copending applications for United States Letters Patent having Serial Nos. 751,651, 751,654 and 751,653, filed of even date, which are respectively entitled "Polyphenolic Polymer Reserving Agents for 'Nitrile Alloy' Fibers"; "Polyphenolic Alkane Reserving Agents for 'Nitrile Alloy' Fibers"; and "Phosphorous-Containing Polyphenolic Reserving Agents for 'Nitrile Alloy' Fibers."

It would be particularly desirable for a reserving agent for "nitrile alloy" fibers to be available that could be employed with great satisfaction for the union-dyeing of blends of "nitrile alloy" fibers with various cellulosic fibers, particularly viscose rayon and cotton, in order to obtain light shades of coloration in the resulting blend with vat and soluble vat dyestuffs. This would provide a beneficial solution to the not inconsiderable problem that on occasion has been encountered in the union-dyeing of blends of "nitrile alloy" fibers with cellulose fibers in order to achieve light or very light shades with vat and soluble vat dyes since, ordinarily, the "nitrile alloy" fiber is found to dye to a noticeably darker shade of coloration in light shades than the cotton or viscose rayon yarn with which it is blended and attempted to be union-dyed with the mentioned two classes of dyestuffs.

Thus, it would be advantageous, and it is the aim and concern of the present invention, to provide "nitrile alloy" fibers altered or modified with respect to their receptivity for dyestuff over a range extending from the capability of such altered forms of "nitrile alloy" fibers to be completely or substantially completely resistant to becoming stained by application of dyestuffs to lesser degrees of resistance, advantageous for purposes of achieving two-toned or union-dyeing, as may be desired, in blends of the "nitrile alloy" fibers with various cellulosic and proteinous fibers, said lesser degrees of resistance to dyestuffs varying through an entire scale, as it were, from slightly to considerable in inverse proportion to their altered degree of dye-receptivity.

It is the principal object of the present invention to provide and make available highly efficacious reserving (or dye resisting) agents specific in their limiting effect or action upon the dye-receptivity of "nitrile alloy" fibers so

as to be useful for the several indicated and related purposes upon and in conjunction with "nitrile alloy" fibers, particularly those comprising polymerized N-vinyl lactam (especially N-vinylpyrrolidone or N-vinyl caprolactam) or polymerized N-vinyl-2-oxazolidinone (including especially the unsubstituted and methyl and ethyl ring substituted species) constituents as dye-receptive adjuvants for the fiber, including unmixed "nitrile alloy" fibers as well as blends of "nitrile alloy" fibers with cellulosic or proteinous fibers and yarn, thread, cord and the like and cloth or fabric constructed from such fibers or fiber blends.

Another object of the invention is to provide, as new and improved articles of manufacture, "nitrile alloy" fibers, including such fibers in unmixed as well as in blended forms and textile articles constructed therefrom, having their degree of dye-receptivity or susceptibility to coloration or staining by dyes and the like controlled by modification or alteration of their normal characteristics in such regard by means of certain dye-resisting agents, as hereinafter more fully delineated, applied to the fibers.

Still an additional object of the invention is to furnish a method or means for controlling the dye-receptivity of "nitrile alloy" fibers in unmixed or blended masses or in various constructed or fabricated textile articles or, as might be otherwise expressed, a new and improved method for dyeing or controlling the dyeing of "nitrile alloy" fibers, especially when they are in blended cellulose or proteinous fiber-containing masses so as to achieve and possible two-tone or union-dyeing effects.

Yet a further object of the invention, one of particular significance, is to furnish "nitrile alloy" fibers in a form in which they can be satisfactorily union-dyed to light shades of coloration with vat and soluble vat types of dyestuffs when they are blended with such cellulosic fibers as cotton and viscose rayon, as well as to furnish an eminently satisfactory method for union-dyeing such blends of "nitrile alloy" fibers to light shades with such dyestuffs using the reserving agent of the present invention in the accomplishment of the intended purpose.

The above indicated objects, and corollary benefits and advantages, may be achieved pursuant to the comprehension and practice of the present invention by applying to a "nitrile alloy" fiber, particularly one of the indicated highly desirable varieties, a minor proportion of from about 0.1 to about 20 percent by weight, based on the weight of the resulting composition and depending upon the extent of dye-resistance or degree of control desired, of a 2,2'-dihydroxy-5,5'-dichlorodiphenyl methane compound, or one of its equivalent close homologues, as a dye reserving or dye resisting agent. As might be anticipated, the degree of control or resistance to dyeing or the extent of modification of the dye-receptivity of the "nitrile alloy" fiber that may be achieved is in proportion to the quantity of the dye reserving or resisting agent that is applied thereto. Complete or practically complete resistance to dyeing and coloration are generally afforded by heavier applications of the agent, such as those in the neighborhood of from about 10 to 20 percent by weight. A partial or appreciably enhanced resistance to dyeing (or decrease in dye-receptivity) of the "nitrile alloy" fiber to an extent or degree that is especially beneficial for achieving two-tone shades in the dyeing or "nitrile alloy" fiber blends may be secured by using a "reserving" quantity of the agent on the fiber that is between about 1.5 or 2 to about 10 percent by weight with the specific effect of the agent again being proportional to the quantity applied. Union-dyeing effects in blends of "nitrile alloy" fibers with cellulosics or proteinous fibers may ordinarily be facilitated by utilizing a "balancing" quantity of the agent between about 0.1 and 1.5 or 2 percent by weight in order to promote excellent shade balancing of all the diverse filamentary components during the dyeing of the blend, especially when the dyestuffs employed have a propensity to build up upon or disproportionately color the "nitrile

alloy" fiber in the blend, as is often the case with certain direct and vat types of dyestuffs when used to dye cellulosic blends of the "nitrile alloy" fibers and certain neutral premetalized types of dyestuffs with proteinous blends.

The agents are remarkably adherescent upon and substantive to the "nitrile alloy" fibers and, once applied, remain on the fiber in a generally permanent manner throughout the normal usages and exposures to which the fiber may be put. The dye reserving or resisting agents have no deleterious effects or influence on the physical or aesthetic characteristics and properties of the fibers on which they are applied and may be employed with impunity in this regard. In addition to utilizing the agents for purposes of establishing or augmenting the resistance to staining by dyestuffs and the like of uncolored "nitrile alloy" fibers, the agents may frequently be employed with considerable benefit upon already dyed or colored articles of the fiber to increase or establish their resistance to undesired staining or additional coloration from various sources. For such purpose a heavy, totally resisting application of the agent may most beneficially be made on the colored fiber. Such stain-proofing treatment, incidentally, may also be made on dyed or otherwise colored "nitrile alloy" fibers that have been pre-treated, prior to dyeing, with lesser, dye-accepting modifying or mere color "reserving" or "balancing" applications or doses of the agent in quantities insufficient to achieve a total or absolute (or practically so) dyeing or coloration-resisting effect. In addition, as is apparent, the reserving agents may also be used with great advantage for producing white effects in fiber mixtures in piece dyeing such as may be accomplished by printing the reserving agents on the "nitrile alloy" cloth or fabric goods being dyed followed by the piece dyeing operation.

The reserving or dye-resisting agents of the present invention, as has been indicated, are capable of achieving good and oftentimes excellent results in restraining the action of practically any type of dyestuff on "nitrile alloy" fibers.

The compound that can be utilized so advantageously as a reserving agent for "nitrile alloy" fibers in the practice of the present invention is 2,2'-dihydroxy-5,5'-dichlorodiphenyl methane, as well as its equivalent close homologs. The mentioned species of the compound is obtainable from the General Aniline & Film Corporation under the trade-designation or trademark "Preventol GDC," a material that, heretofore, has been widely employed as a fungicide. "Preventol GDC" can be employed as a dye-reserving or resisting agent for practically all classes of dyestuffs, including vat and soluble vat types when it is utilized in sufficiently high concentrations in its application on the fiber. Furthermore, excellent union-dyeing of blends of "nitrile alloy" fibers with cellulosics, such as cotton and viscose rayon, to light shades of coloration using vat and soluble vat dyestuffs may be readily accomplished by using a lesser or shade balancing quantity of the reserving agent in the application thereof on the fibers. In this way, the dyeability of the "nitrile alloy" is balanced, or brought in line, with that of the cotton or viscose rayon for purposes of achieving attractively light or so-called "pastel" shades in union-dyeings with vat and soluble vat dyestuffs.

It is advantageous for the applying formulation or composition of the dye-resisting agent that is utilized for deposition of the latter upon the "nitrile alloy" fibers to contain between about 0.1 and 20 percent by weight, based on the weight of the fiber, of the dissolved or dispersed dye-resisting agent, depending on the precise quantity of the agent that may be desired to be deposited on the fiber. The actual concentration of the agent with respect to the liquid medium from which it is applied may be much less than the above-indicated values. Since the agents are highly substantive to the "nitrile alloy" fibers, their precise concentration with respect to the liquid vehicle in the applying formulation is relatively immaterial.

terial. Generally, the applying formulation of the dye-resisting agent is found to be completely, or substantially completely, exhausted of the agent so that its precise concentration in the liquid vehicle is not an essential criticality. In most instances, however, it is unnecessary for the applying formulations to contain more than about 5 percent of the dye-resisting agent, based on the weight of the dry fiber (o.w.f.) and depending on the type of dyeing procedure used. Suitable application of the dye-resisting agent may be made when the liquor-to-fiber ratio of the applying formulation to the "nitrile alloy" fiber being treated is between about 5 and 30 parts of the former to each part by weight of the fiber. More often it is advantageous for such liquor-to-fiber ratio to be between about 5:1 to 15:1, respectively.

Various techniques may be utilized for preparing suitable applying formulations of the dye reserving or resisting agent if not obtained in such form (as generally merchandised). Usually, as is apparent, it is advantageous to apply it from an aqueous liquid dispersion or solution. Such a dispersion may be prepared by making a preliminary solution of the dye-resisting agent in a liquid in which it is soluble (such as aqueous, sodium hydroxide, lower aliphatic alcohols or ketones) and then diluting the initially prepared solution with the desired quantity of water to prepare the final formulation. Most advantageously, especially when the reserving agents are used in conjunction with dyeing treatments on the fiber, the applying formulation may be prepared and employed directly as part of the liquid vehicle or bath in which the fibers are contained during the dyeing. Thus, if it is intended to apply the resisting agent prior to dyeing, the applying formulation may be prepared and used for deposition of the resisting agent as well as to constitute the body of the dye bath in which the dyeing treatment is accomplished. In an analogous manner, the dye-resisting agent may be added to dyed fibers in intermediate stages or after completion of dyeing by incorporating it in the dye bath during the dyeing treatment or after the dyeing has been accomplished, depending upon the particular purpose for which the agent is being employed.

In addition, somewhat in the manner of conventional textile finish application, the dye resisting agent may be applied to the fibers from the applying formulations by distributing the formulation directly to a running strand of the "nitrile alloy" fiber being treated using a liquid jet or spray of the formulation. If desired, applying rollers and equivalent devices may be utilized for such purpose. When the dye-resisting agent is being applied to "nitrile alloy" articles, including articles prepared from fiber blends that are in the form of cloth or fabric, the application may be made during any stage of manufacture or dyeing of such article using procedures analogous to those herein described and demonstrated. When cloth and fabric are being treated, it may frequently be most convenient for the application to be made in a manner analogous to conventional padding treatments.

In order to further illustrate the invention, but without being limited thereto or restricted thereby, the following examples are given wherein, unless otherwise indicated, all parts and percentages are to be taken on a weight basis.

Example 1

About 250 grams each of a uniform fiber blend of a "nitrile alloy" fiber and cotton was prepared by mixing in a package machine. The "nitrile alloy" fiber was three denier, 1½ inch staple length. It was comprised of polyacrylonitrile containing uniformly incorporated therein, as a dye-assisting adjuvant, about 8 percent on the weight of the fiber (o.w.f.) of poly-N-vinyl-2-pyrrolidone having a Fikentscher K-value of about 55. Mesa Acala cotton was used in the blend. The blended fibers were scoured at 95° C. in about 5000 ml. of aqueous solution containing about 1 percent (o.w.f.) of a non-ionic detergent and 1 percent (o.w.f.) tetra sodium pyrophosphate. The

scouring was continued for about one hour, after which the fibers were removed and placed in about a 5000 ml. volume of a 3 percent o.w.f. aqueous solution of "Preventol GDC" at 50° C. The fiber blend was maintained in the solution at the same temperature for about 5 minutes, after which there was added about 0.5 percent o.w.f. of Vat Printing Brown HRR suprafix paste (no color index), a vat dyestuff. Pigmenting with the dyestuff was continued at 50° C. for about 15 minutes. After the pigmenting, about 4 percent o.w.f. sodium hydroxide and 4 percent o.w.f. sodium hydrosulfite were added to the dye bath. The dyeing was continued for 30 minutes. The fiber blend was rinsed thoroughly with water and oxidized for 15 minutes at 80° C. in about 5000 ml. of an aqueous solution containing about 2 percent of hydrogen peroxide (o.w.f.) (35 percent concentration) and 1 percent (o.w.f.) of 56 percent acetic acid. After the oxidation, the blend was rinsed thoroughly with water and scoured for about half an hour at 95° C. in a 1 percent solution of a non-ionic detergent. An excellent union-dyeing of the "nitrile alloy" and cotton in the blend was obtained with the dyed product having an attractive light brown shade of coloration. When the foregoing was repeated, excepting to eliminate the application of the dye-resisting agent, the "nitrile alloy" fibers in the resulting dyed blend were obtained with a shade of coloration that was noticeably deeper than that of the cotton.

Example 2

The procedures of the first example was repeated, excepting to apply 5 percent o.w.f. of the "Preventol GDC" after the scouring, and to dye the treated blend with 0.25 percent Cibane Blue GF micro powder (Color Index Vat Blue 6), a vat dyestuff using a dye bath to fiber ratio of about 10:1. The "nitrile alloy" fiber in the blend was found to have been left in a practically undyed condition, whereas the cotton was dyed to an attractive shade of very light blue. In contrast, when the foregoing procedure was repeated, excepting to eliminate the treatment of the blend with the dye-resisting agent, both the "nitrile alloy" and the cotton were dyed with the vat dyestuff.

Example 3

About 5 grams of 3 denier "nitrile alloy" fiber (same as in Example 1) in 20s/1 staple length form and cotton (40/2) were uniformly blended and scoured in the manner set forth in the first example at 90° C. After the scouring they were rinsed thoroughly with water, then treated with about 150 ml. of an aqueous solution of "Preventol GDC" containing 2 percent o.w.f. of the dye-resisting agent. The treatment was conducted for 20 minutes at 70° C. After this time, about 0.25 percent o.w.f. Indigosol Brown 1BR (Color Index Vat Brown I), a soluble vat dyestuff, was added to the liquor containing the blend and run for 15 minutes at the indicated temperature. At this point, about 10 grams of Glauber's salt was added to the dye bath over a 15 minute period and the dyeing continued for an additional 15 minutes. The fiber blend was then removed from the dye bath and oxidized in a fresh bath having about a 10:1 liquor-to-fiber ratio and containing about 1 percent o.w.f. of sodium bichromate, 2 percent o.w.f. of ammonium thiocyanate and about 20 percent o.w.f. of concentrated sulfuric acid. The oxidation was conducted at 95° C. for a 30 minute period. After the oxidation the fibers were rinsed thoroughly with water, scoured at 95° C. for 30 minutes with a non-ionic detergent, rinsed again and dried. An excellent union-dyeing of both the "nitrile alloy" and cotton fibers in the blend was obtained with the resulting product having a uniform and attractive tan shade of coloration, even under microscopic examination.

Example 4

When the procedures of each of the first three examples are repeated excepting to substitute viscose rayon yarn

for the cotton in the blend, similar excellent results are obtained.

Example 5

When the initial procedures of each of the preceding examples are repeated, including experiments with both cotton and viscose rayon blends with the "nitrile alloy," excepting to apply between about 5 and 20 percent o.w.f. of the "Preventol GDC" on the fiber as a dye-resisting agent, substantially complete resistance to becoming colored by either direct, acid, acid premetallized, soluble vat and vat dyestuffs, among others, is achieved on the "nitrile alloy" fibers.

Example 6

About 5 grams of a uniform 50:50 blend of a "nitrile alloy" fiber and wool was prepared. The "nitrile alloy" fiber was of the same chemical composition as described in the first example, excepting that it was obtained in the form of 2 denier, bright 3-inch staple lengths. The wool was 3 inch Australian 64s. The blend of fibers was placed in a bath having a 30:1 liquor-to-goods ratio. Five percent (o.w.f.) "Preventol GDC" was added to the bath at 40° C. along with 2 percent (o.w.f.) "Igepon T33," a conventional synthetic detergent surface active dispersing agent. This was run for 20 minutes. Sufficient monobasic sodium phosphate (NaH_2PO_4) was then added slowly to bring the pH to 7. After this adjustment, about 5 percent (o.w.f.) ammonium sulfate was added to the bath followed by milling using 0.5 percent Polar Brilliant Blue Raw (Color Index Acid Blue 80), an acid dyestuff. The temperature was then brought up to 100° C. and the dye bath run for 2 hours at this temperature. After the dyeing, the blend of fibers was cold rinsed with water. The "nitrile alloy" fibers in the blend were completely undyed, whereas the wool had taken on the dyestuffs to a deep and level shade of coloration. In comparison, when the foregoing is repeated without use of the reserving agent, both of the fibers in the blend are deep-dyed by the dyestuff.

Example 7

The procedure of Example 6 was identically duplicated down to the point of adjustment of the bath to pH 7 with monobasic sodium phosphate. After this, the bath was set with 4 percent (o.w.f.) of 56 percent concentrated acetic acid at a temperature of 40° C. At this point, about 0.5 percent (o.w.f.) of a chrome dye was added to the bath. The dyestuff employed was "Omega Chrome Green B" (Color Index Mordant Green 9). The temperature was raised to 100° C. and the bath run for an additional 30 minutes, at which time another 4 percent (o.w.f.) of the same acetic acid reagent was added, whereupon the material was run for another hour. After the termination of this time, the goods were rinsed, then placed in a fresh bath having the same liquor-to-goods ratio that was made up with 8 percent (o.w.f.) of the acetic acid and 0.3 percent (o.w.f.) sodium dichromate at 60° C. The new bath was then heated to 100° C. and run for 45 minutes, followed by rinsing. At the termination of this procedure, the "nitrile alloy" fiber in the blend was found to have been completely white and undyed, whereas the wool had assumed a good green color. In the absence of the "Preventol GDC" at the beginning of the treatment, both the "nitrile alloy" and the wool fiber are deeply dyed by the dyestuff.

Example 8

When the procedures of the foregoing examples are duplicated, excepting to employ (in place of the therein utilized "nitrile alloy" yarn) fibers containing either poly-N-vinyl caprolactam, poly-N-vinyl-2-oxazolidinone, poly-N-vinyl-5-methyl-2-oxazolidinone or poly-N-vinyl-3-morpholinone as the dye-accepting adjuvant in place of the PVP in the "nitrile alloy" fiber (using about the same quantity of the additive for the purpose) similar excellent results are achieved.

Results similar to the foregoing may also be obtained when "nitrile alloy" fibers are employed containing other of the beneficial alloying components mentioned in the foregoing. Excellent results may also be achieved when the resisting agents are applied on unmixed or unblended "nitrile alloy" fibers for purposes and applications where such technique and manner of treatment is desirable and indicated. Commensurate results may likewise be achieved with other blends of the "nitrile alloy" fibers, including blends with cellulose other than cotton or viscose rayon yarn (such as cuprammonium rayon yarn, cellulose acetate and the like cellulose esters and other cellulose fibers of natural or synthetic or artificial origin) as well as blends of the "nitrile alloy" fibers with various proteinous fibers of natural or synthetic origin, including wool, silk fibers, zein-protein fibers (such as those that are commercially available under the trade-name "Vicara") feather-keratin, casein fibers, protein fibers and the like proteinous or so-called Azlon fibers of natural, artificial, regenerated, or reconstituted origin.

As has been indicated in the foregoing, the "nitrile alloy" fibers are comprised essentially of the mentioned acrylonitrile polymer base which has been modified or alloyed with beneficial additaments or constituents which are adapted and calculated to provide the fiber product with its peculiar and unusually advantageous properties. Various beneficial additaments or constituents that are capable of securing the desirable characteristics of which the "nitrile alloy" fiber is possessed may be any of several diverse types. For example, the beneficial constituent may be derived from and originate with a monomer or mixture of monomers, capable of being converted to a dye-receptive and possibly otherwise functional polymer product, which is graft or block copolymerized to and upon the already formed (and, with advantage, already fabricated) acrylonitrile polymer base. Alternatively, and with equal advantage, the beneficial constituent may be a dye-receptive and possibly otherwise functional, polymeric product with which the essential acrylonitrile base is graft or block copolymerized by graft copolymerization of acrylonitrile or an acrylonitrile monomer mixture on or with the already formed functional polymer in order to furnish the fiber-forming polymer product of which the "nitrile alloy" fiber is composed. Or, as a suitable and frequently quite satisfactory alternative, the already formed beneficial additaments or constituents in the "nitrile alloy" fiber may be in the nature of polymeric adjuvants that are physically blended and intimately incorporated by any of several suitable procedures with the essential acrylonitrile polymer base. Such adjuvants may be homopolymeric, copolymeric or graft copolymeric substances which serve to augment at least the dyeability of the normal difficult (if not impossible) to dye acrylonitrile polymer base.

Amongst the most beneficial and advantageous of the "nitrile alloy" fibers are those that are comprised of the essential acrylonitrile polymer base, particularly polyacrylonitrile, in which there has been intimately and permanently or substantially permanently incorporated minor proportions of from about 1 or so up to about 20 or so percent by weight, based on the weight of the "nitrile alloy" composition, of any of the beneficial additaments or constituents adapted to serve the desired purpose and provide the beneficial result. Generally, such beneficial additaments are employed primarily as dye-assisting adjuvants or components. Advantageously, they may be the polymerized products of such azotic monomers, or mixtures thereof, as the several N-vinyl lactams including such broadly related products as the N-vinyl-3-morpholinones; the N-vinyl-2-oxazolidinones; and certain of the N-vinyl-N-methyl-alkylsulfonamides. Thus, the "nitrile alloy" may be comprised of the acrylonitrile polymer base that is prepared by graft or block copolymerization of acrylonitrile or an acrylonitrile-containing monomer mixture upon a minor proportion of an already

formed polymer derived from any of the indicated varieties of azotic monomers or their mixtures. Or, as mentioned, it may consist of a graft copolymer product of any of the indicated varieties of azotic monomers on an already formed and preferably already fabricated acrylonitrile polymer base. Advantageously, and frequently, with consummate suitability, the "nitrile alloy" fiber may be comprised of the acrylonitrile polymer base in which there is permanently incorporated by physical blending a minor proportion of any of the polymer products from the specified azotic monomers or mixtures thereof, primarily as dye-assisting adjuvants.

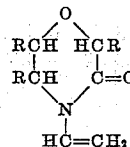
Such species of "nitrile alloy" fibers are capable of being accurately described as synergetic and anisotropic clathrates that are composed of a hydrophobic polymer in combination with a hydrophilic polymer. In such varieties of the "nitrile alloy" fibers (as well as in other of the forms in which they may be obtained) there is a mutually enhancing cooperative union of a highly crystalline polymer which provides strength, durability, wrinkle recovery and high melting point in the fibers with an usually non-ionic polychelate that provides dye-receptivity as well as moisture regaining powers for the fiber and other aesthetic characteristics that lend to the wearing comfort of textile goods manufactured from the fiber. The "nitrile alloy" fibers have been described by G. W. Stanton in an article entitled "Zefran" appearing in the Textile Research Journal, volume XXVII, No. 9, for September 1957, pp. 703-712. They have also been recognized as a distinct class of man-made synthetic textile fibers in Textil Organon, September 1956, at pages 129-130.

As indicated, the adjuvant or beneficial constituent in the "nitrile alloy" fiber may be homopolymeric in nature or it may be a straight copolymer of any of the azotic monomers specified with other mono- and polyfunctional monomers. Adjuvants of this variety are ordinarily physically blended with the essential acrylonitrile polymer base in order to secure the desired intimate incorporation of the beneficial constituent and the resulting alloying effect in the fiber. Likewise, there may be similarly utilized for physical blending purposes adjuvants or additaments that are graft copolymeric in nature and which consist of various monomers that are graft copolymerized on substrates consisting of polymers of any of the indicated azotic monomers, such as poly-N-vinyl-lactam substrates; poly-N-vinyl-2-oxazolidinone substrates and poly-N-vinyl-N-methyl-alkylsulfonamide substrates. Similarly, just as suitably, graft copolymeric additaments may be provided and employed when they consist of any of the specified or closely related azotic monomers (such as N-vinyl lactam monomers, N-vinyl-2-oxazolidinone monomers and N-vinyl-N-methyl alkylsulfonamide monomers) graft copolymerized on other functional polymer substrates.

It is usually beneficial for the polymer products of the azotic functional monomers to be present as the beneficial component in "nitrile alloy" fibers in an amount that is in the neighborhood or range of from about 5 to 15 percent by weight, based on the weight of the "nitrile alloy" composition. It is frequently quite desirable to employ a homopolymeric N-vinyl lactam polymer, such as poly-N-vinylpyrrolidone (which may also be identified as poly-N-vinyl-2-pyrrolidone or, with varied terminology, poly-N-vinyl-2-pyrrolidinone), poly-N-vinyl caprolactam, or somewhat related thereto, a poly-N-vinyl-3-morpholinone; or a homopolymeric N-vinyl-2-oxazolidinone or poly-N-vinyl-5-methyl-2-oxazolidinone; or a homopolymeric N-vinyl-methylalkylsulfonamide polymer such as homopolymeric N-vinyl-N-methyl-methylsulfonamide; as the polymeric adjuvant that is blended with the essential acrylonitrile polymer base in the "nitrile alloy" composition. When physically blended "nitrile alloy" products are prepared that utilize, as the beneficial additament or constituent, copolymeric or graft copolymeric products

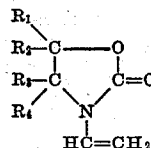
of the indicated azotic monomers, it is usually beneficial for the polymeric adjuvants that are employed to be those which are comprised of at least about 50 percent or even as much as 80 or more percent by weight of the products of the indicated constituents derived from the azotic monomers.

In addition to products of N-vinyl-pyrrolidone or N-vinyl caprolactam, other of the N-vinyl (or 1-vinyl) lactams which may be utilized include any of those (or their mixtures) that have been described or which are involved in U.S. Patents Nos. 2,265,450; 2,355,454 and 2,371,804. Particular mention may also be made of N-vinyl-5-methyl-pyrrolidone; N-vinyl-3,3-dimethyl gamma valerolactam; and N-vinyl piperidone. Particular mention may also be made of somewhat related products derived in any of the ways described from N-vinyl-3-morpholinones of the structure:



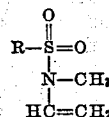
wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon alkyl radicals, 6 to about 10 carbon aryl radicals and equivalents thereof.

Similarly, besides unsubstituted N-vinyl-2-oxazolidinone, other N-vinyl (or 3-vinyl)-2-oxazolidinone products which may be used as polymeric adjuvants include those derived from monomers represented by the formula:



in which at least one of the substituent R_1 , R_2 , R_3 or R_4 groups, when it is not hydrogen, may be a 1 to about 4 carbon atom alkyl radical or a 6 to about 10 carbon atom aryl radical or their equivalents. Typical of such monomers may be mentioned N-vinyl-5-methyl-2-oxazolidinone; N-vinyl-5-chloromethyl-2-oxazolidinone; N-vinyl-4,5-dimethyl-2-oxazolidinone, N-vinyl-5-ethyl-2-oxazolidinone; N-vinyl-5-phenyl-2-oxazolidinone; and the like.

The N-vinyl-N-methyl-alkylsulfonamide monomers whose polymeric products may be advantageously utilized for the "nitrile alloys" include those represented by the formula:



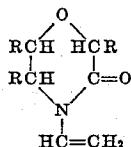
wherein R is hydrogen, a 1 to about 4 carbon alkyl radical, a 6 to about 10 carbon aryl radical or some equivalent thereof.

Suitable "nitrile alloy" products may also be manufactured from other beneficial additaments or components that are more or less equivalent to those derived from the azotic monomers indicated in the foregoing. Thus, other varieties of N-heterocyclic monomers more or less similar or related to the specified N-2-propenyl types and analogous related azotic compounds may frequently be employed in combination with or to replace the several beneficial additaments or constituents that have been delineated.

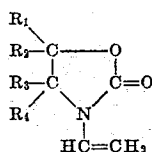
What is claimed is:

1. A synthetic textile fiber which is characterized in having its normal receptivity to dyestuffs modified so as to have dye-resisting characteristics, said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essen-

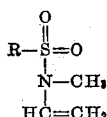
tially of (A1) between about 80 and about 99 weight percent, based on dry fiber weight, of a fiber-forming acrylonitrile addition polymer with (A2) between about 20 and about 1 weight percent, based on dry fiber weight, of an azotic polymeric dye-assisting adjuvant selected from the group consisting of addition polymers of at least about 50 weight percent, based on the weight of the azotic polymer, of (A2a) N-vinyl lactam monomers; (A2b) n-vinyl-3-morpholinone monomers of the structure:



wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon atom aryl substituents; (A2c) N-vinyl-2-oxazolidinone monomers of the structure:



in which R₁, R₂, R₃ and R₄ are independently selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon atom aryl substituents; (A2d) N-vinyl-N-methyl-alkyl-sulfonamide monomers of the structure:



wherein R is selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon atom aryl substituents; and (A2e) mixtures thereof; (B) fiber-forming graft copolymers comprised essentially of (B1) between about 80 and about 99 weight percent, based on dry fiber weight, of a pre-formed fiber-forming acrylonitrile addition polymer substrate with graft copolymerized substituents thereon of (B2) between about 20 and about 1 weight percent, based on dry fiber weight, of addition polymerized azotic monomer substituents of at least about 50 weight per cent, based on the weight of graft copolymerized substituent, of (B2a) N-vinyl lactam monomers; (B2b) said N-vinyl-3-morpholinone monomers; (B2c) said N-vinyl-2-oxazolidinone monomers; (B2d) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (B2e) mixtures thereof; and (C) fiber-forming graft copolymers comprised essentially of (C1) between about 80 and 99 weight percent, based on dry fiber weight, of acrylonitrile graft copolymerized on (C2) between about 20 and about 1 weight percent, based on dry fiber weight, of a pre-formed, dye-assisting, azotic addition polymer substrate of at least about 50 weight percent, based on the weight of said substrate, of (C2a) N-vinyl lactam monomers; (C2b) said N-vinyl-3-morpholinone monomers; (C2c) said N-vinyl-2-oxazolidinone monomers; (C2d) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (C2e) mixtures thereof, said fiber containing as a dye reserving and resisting agent effective against direct, acid and vat dyestuffs between about 0.1 and 20 percent by weight, based on the weight of the fiber, of 2,2'-dihydroxy-5,5'-dichlorodiphenyl methane.

2. The treated fiber of claim 1 containing between about 0.1 and about 2 percent by weight of said reserving agent and characterized in having relatively slight resistance to becoming stained upon contact with dyestuffs.

3. The treated fiber of claim 1 containing between about 1.5 and about 10 percent by weight of said reserving agent and characterized in having a moderate reserving action to becoming stained upon being contacted with dyestuffs.

4. The treated fiber of claim 1 containing between about 10 and about 20 percent by weight of said reserving agent and characterized in having a substantially complete resistance to becoming stained upon contact with dyestuffs.

5. The treated fiber of claim 1 contained in a blend of fibers with cellulosic fibers.

6. A blend of fibers in accordance with the blend set forth in claim 5, wherein said cellulosic fibers are cotton.

7. The treated fiber of claim 1 contained in a blend of fibers with proteinous fibers.

8. A blend of fibers in accordance with the blend set forth in claim 7, wherein said proteinous fibers are wool.

9. The treated fiber of claim 1, wherein said synthetic fiber contains polymerized N-vinyl lactam.

10. The treated fiber of claim 1, wherein said synthetic fiber contains polymerized N-vinyl-2-oxazolidinone monomer.

11. The treated fiber of claim 1, wherein said synthetic fiber contains polymerized N-vinyl-3-morpholinone monomer.

12. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinyl-2-pyrrolidone as a dye-assisting adjuvant.

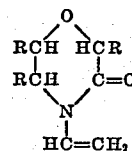
13. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinylcaprolactam as a dye-assisting adjuvant.

14. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinyl-5-methyl-2-oxazolidinone as a dye-assisting adjuvant.

15. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinyl-2-oxazolidinone as a dye-assisting adjuvant.

16. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinyl-3-morpholinone as a dye-assisting adjuvant.

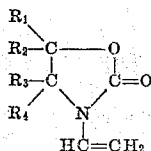
17. Treatment for a synthetic fiber to reduce its receptivity to direct, acid and vat dyestuffs, said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essentially of (A1) between about 80 and about 99 weight percent, based on dry fiber weight, of a fiber-forming acrylonitrile addition polymer with (A2) between about 20 and about 1 weight percent, based on dry fiber weight, of an azotic polymer dye-assisting adjuvant selected from the group consisting of addition polymers of at least about 50 weight percent, based on the weight of the azotic polymer, of (A2a) N-vinyl lactam monomers; (A2b) N-vinyl-3-morpholinone monomers of the structure:



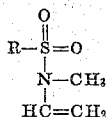
wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon

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atom aryl substituents; (A2c) N-vinyl-2-oxazolidinone monomers of the structure:



in which R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon atom aryl substituents; (A2d) N-vinyl-N-methyl-alkyl-sulfonamide monomers of the structure:



wherein R is selected from the group consisting of hydrogen, 1 to about 4 carbon atom alkyl substituents and 6 to about 10 carbon atom aryl substituents; and (A2e) mixtures thereof; (B) fiber-forming graft copolymers comprised essentially of (B1) between about 80 and about 99 weight percent, based on dry fiber weight, of a pre-formed fiber-forming acrylonitrile addition polymer substrate with graft copolymerized substituents thereon of (B2) between about 20 and about 1 weight percent, based on dry fiber weight, of addition polymerized azotic monomer substituents of at least about 50 weight percent,

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based on the weight of graft copolymerized substituent, of (B2a) N-vinyl lactam monomers; (B2b) said N-vinyl-3-morpholinone monomers; (B2c) said N-vinyl-2-oxazolidinone monomers; (B2d) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (B2e) mixtures thereof; and (C) fiber-forming graft copolymers comprised essentially of (C1) between about 80 and 99 weight percent, based on dry fiber weight, of acrylonitrile graft copolymerized on (C2) between about 20 and about 1 weight percent, based on dry fiber weight, of a pre-formed, dye-assisting, azotic addition polymer substrate of at least about 50 weight percent, based on the weight of said substrate, of (C2a) N-vinyl lactam monomers; (C2b) said N-vinyl-3-morpholinone monomers; (C2c) said N-vinyl-2-oxazolidinone monomers; (C2d) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (C2e) mixtures thereof, which treatment comprises applying to the fiber between about 0.1 and 20 percent by weight on the weight of the fiber of 2,2'-dihydroxy-5,5'-dichlorodiphenyl methane.

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