United States Patent Office 2,931,697 Patented Apr. 5, 1960

2,931,697

POLYPHENOLIC ALKANE RESERVING AGENTS FOR ACRYLONITRILE POLYMER BASE FIBERS

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No Drawing. Application July 29, 1958
Serial No. 751,654

22 Claims. (Cl. 8—21)

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 paradoxal 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 cellulosics 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 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 directly dyed with the same dyestuff or coloring agent or combination of dyestuffs or coloring agents in the same dyeing treatment performed in the same or separate sequential stages or operations 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.

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 dyestuffs 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-vinylcaprolactam) 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 in 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 or "nitrile alloy" fibers, especially when they are in blended cellulose or proteinous fiber-containing masses so as to achieve and possibilitate two-tone or union-dyeing effects.

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 of degree of control desired, of a certain variety of polyphenolic alkane compound, as

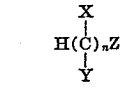
hereinafter more fully illustrated, as a dye reserving or dye-resisting agent. As might be anticipated, the degree of control or resistance to dyeing or the extent of modification of the dye-receptivity of the "nitrile alloy" fiber that may be achieved is in proportion to the quantity of the dye reserving 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 of "nitrile alloy" fiber blends may be secured by using a "reserving" quality of the agent on the fiber that is between about 1.5 to 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 disporportionately color the "nitrile alloy" fiber in the blend, as is often the case with certain direct or after-treated direct types of dyestuffs when used to dye cellulosic blends of the "nitrile alloy" fibers and certain acid types of dyestuffs with proteinous blends. In any case, the precise quantity of the reserving agent that is necessary to apply for any particular purpose can be quickly and readily determined by control testing techniques.

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 excessive deleterious effect or intolerable influence on the physical aesthetic characteristics and properties of the fibers on which they are applied and may ordinarily be employed for many of a wide variety of uses with relative impurity 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 of 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 excellent results in restraining the action of direct and certain acid dyes on "nitrile alloy" fibers.

The polyphenolic alkane dye reserving or resisting agents that are used so advantageously in conjunction with "nitrile alloy" fibers in the practice of the present invention consist essentially of a polymeric structure having a straight chain of 2 to about 6 carbon atoms and

which contains from 3 to about 6 para-hydroxy phenyl groups in its constitution. Such compounds as 1,1,2,2-tetrakis-p-hydroxy-phenyl ethane and 1,1,2,2-tetrakis-p-hydroxy-phenyl propane may be used with especial benefit as the polyphenolic alkane reserving agents in the practice of the present invention, as may such other materials as 2,2,4,4-tetrakis-para-hydroxy-phenyl pentane; 2,2,4,4-tetrakis-para-hydroxy-phenyl hexane; tris-p-hydroxy-phenyl methane; 2,3,3-tris-p-hydroxy-phenyl butane; 2,2,4,4,6,6-hexakis-p-hydroxy-phenyl hexane; and the like. As is apparent, the polyphenolic alkane substances that may be employed as reserving agents in the practice of the invention are of the general structure:



(I)

wherein X, Y and Z are independently selected from the group consisting of hydrogen and p-hydroxy phenyl radicals with the limitation that a total of not less than about 3 and not more than about 6 p-hydroxy phenyl groups can be present in the compound; and wherein *n* is a number having an average value from 1 to about 6.

It is advantageous for the applicating formulation or composition of the dye-resisting agent that it 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 upon 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 applicating formulation is relatively immaterial. Generally, the applicating 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 applicating formulations to contain more than about 5 percent of the dye-resisting agent, based on the weight of the dry fiber 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 applicating formulation to the "nitrile alloy" fiber being treated is between about 1 and 100 parts of the former to each part by weight of the fiber. More often it is advantageous for such liquor-to-fibers ratio to be between about 2:1 to 50:1, respectively.

Various techniques may be utilized for preparing suitable applicating formulations of the dye reserving or resisting agent. 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 or preparatory solution of the dye-resisting agent in a liquid in which it is soluble (such as lower aliphatic alcohols, i.e., methanol, ethanol, etc., ketones, aqueous sodium hydroxide or other caustic solutions) 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 applicating 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 applicating 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 agents may be added to dyed fibers in intermediate stages or after completion of dyeing by incorcorporating them 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 agents may be applied to the fibers from their applicating 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, applicating rollers and equivalent devices may be utilized for such purpose. When the dye-resisting agents are 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

A uniform blend of about 100 parts of viscose rayon fibers and 100 parts of "nitrile alloy" fibers were treated by uniform application thereto of about 5 parts of a dye-resisting agent consisting of 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane. The "nitrile alloy" synthetic fibers in the blend were about 3 denier fibers in staple lengths of about 1½ inches. They were comprised of polyacrylonitrile in which there was uniformly incorporated about 8 percent on the weight of the fiber (O.W.F.) of poly-N-vinyl-2-pyrrolidone (PVP) having Fikentscher K-value of about 55. The viscose rayon yarn was a semi-dull yarn having a staple length of about 1½ inches and a denier of about 3. The dye-resisting agent was applied on the blended fiber mixture by first dissolving the polyphenolic alkane in about ½ of its weight of Na_2CO_3 (anhydrous) and 20 parts of water and then diluting the initial caustic solution with 6,000 parts of water. The application of the resisting agent to the fiber blend was made by immersing the blend in the finally resulting dilute solution of the resin for 20 minutes at 70° C. Without removing the fiber blend from the applicating solution of the resisting agent, about one part of Diphenyl Red 4B Supra (Color Index Direct Red 2), a direct dyestuff, was added to the treating liquor and the system agitated for about one hour while being maintained at a temperature of about 70° C. During the dyeing, about 20 parts of sodium chloride were gradually added to the system. At the termination of the dyeing, the treated blend was removed from the dyestuff-containing system, rinsed and dried. The "nitrile alloy" fiber was left entirely unstained and in a completely white condition. The viscose rayon component, however, was dyed to a deep and level shade of coloration. In contrast, when the foregoing was repeated, excepting to eliminate the preliminary application of the reserving agent, a full depth dyeing of both fibers in the blend was obtained.

Example 2

The procedure of the first example is repeated in several separate duplications excepting to use "nitrile alloy" fibers prepared from analogous polymer blends of polyacrylonitrile with poly-N-vinyl-2-caprolactam; poly-N-vinyl-2-oxazolidinone (K–13) poly-N-vinyl-5-methyl-2-oxazolidinone (K–29) and poly-N-vinyl-3-morpholinone (K–60) in place of the PVP as the dye-assisting adjuvants. Identical results are obtained in each case.

Example 3

Using the same "nitrile alloy" fiber as in the first example, one part of tris(p-hydroxyphenyl) methane was dissolved in 10 parts of water containing ½ part sodium carbonate anhydrous at 85° C. Two and one-half parts of a "nitrile alloy" knit goods and two and one-half parts cotton plain weave cloth (prescoured in 1 percent Igepal CA solution) were treated in a bath containing 150 parts liquid with 4 percent O.W.F. reserving agent, at 50° C. in a Laundrometer. One percent Diphenyl Red 4B Supra (Color Index Direct Red 2) was added to the bath and run at 50° C. for one hour. The cotton was dyed deep red while the "nitrile alloy" remained white.

Identical results were obtained using 1,1,2,2-tetrakis (4-hydroxyphenyl) ethane as the reserving agent.

Identical results were obtained using 1,1,2,2-tetrakis-p-hydroxyphenyl propane as the reserving agent.

Identical results were obtained using 2,2,4,4-tetrakis-p-hydroxyphenyl pentane as the reserving agent.

Example 4

Fifty-fifty "nitrile alloy"-cotton blend (using the same "nitrile alloy" as above) striped knit goods were treated with 1,1,2,2-tetrakis-p-hydroxyphenyl ethane in a manner identical to Example 3 above, using Diphenyl Red 4B Supra, except that 0.8 percent and 1.6 percent O.W.F. levels of the reserving agents were employed. Results were the same as in Example 3 for both concentrations.

Example 5

Example 4 was repeated using 1 percent Benzo Blue RWA (Color Index Direct Blue 22), a direct dye. The cotton dyed a deep blue, and the "nitrile alloy" remained white, at both 0.8 percent and 1.6 percent reserve agent levels.

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 and when any other of the polyphenolic alkane reserving agents indicated to be within the scope of the invention are utilized in place of those specifically illustrated. 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 cellulosics 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 normally difficult (if not impossible) to dye acrylonitrile polymer base.

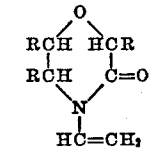
Amongst the most beneficial and advantageous of the "nitrile alloy" fibers are those that are comprised of the essential acrylonitrile polymer base, particularly polyacrylonitrile, in which there has been intimately and permanently or substantially permanently incorporated minor proportions of from 1 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-2-morpholinones; the N-vinyl-2-oxazolidinones; and certain of the N-vinyl-N-methyl-alkyl-sulfonamides. 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 in 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 chathrates 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 alkyl-sulfonamide monomers graft copolymerized on other functional polymer substrates.

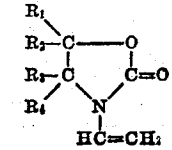
It is usually beneficial for the polymer products of the azotic functional monomers to be present as the beneficial component in "nitrile alloy" fibers in an amount that is in the neighborhood or range of from about 5 to 15 percent by weight, based on the weight of the "nitrile alloy" composition. It is frequently quite desirable to employ a homopolymeric N-vinyllactam 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:



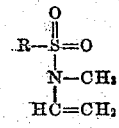
wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon alkyl radicals, 6 to about 10 carbon aryl radicals and equivalents thereof.

Similarly, besides unsubstituted N-vinyl-2-oxazolidinone, other N-vinyl (or 1-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 substituents 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:

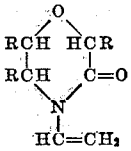


wherein R is hydrogen, a 1 to about 4 carbon alkyl radical, a 6 to about 10 carbon aryl radical or some equivalent thereof.

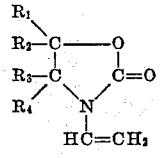
Suitable "nitrile alloy" products may also be manufactured from other beneficial additaments or components that are more or less equivalent to those derived from the azotic monomers indicated in the foregoing. Thus, other varieties of N-heterocyclic monomers more or less similar or related to the specfied 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:

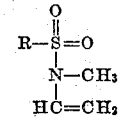
1. A synthetic textile fiber which is characterized in having its normal receptivity to dyestuffs modified so as to have dye-resisting characteristics, said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essentially of (A1) between 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 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 (A2*a*) N-vinyl lactam monomers; (A2*b*) 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; (A2*c*) 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; (A2*d*) N-vinyl-N-methyl-alkylsulfonamide 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 (A2*e*) mixtrures 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, based on the weight of graft copolymerized substituent, of (B2*a*) N-vinyl lactam monomers; (B2*b*) said N-vinyl-3-morpholinone monomers; (B2*c*) said N-vinyl-2-oxazolidinone monomers; (B2*d*) said N-vinyl-N-methyl-alkylsulfonamide monomers and (B2*e*) 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 (C2*a*) N-vinyl lactam monomers; (C2*b*) said N-vinyl-3-morpholinone monomers; (C2*c*) said N-vinyl-2-oxazolidinone monomers; (C2*d*) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (C2*e*) mixtures thereof, said fiber containing as a dye reserving and resisting agent effective against direct and acid dyestuffs between about 0.1 and 20 percent by weight, based on the weight of the fiber, of a compound having the formula:

(I)

wherein X, Y and Z are independently selected from the group consisting of hydrogen and p-hydroxy phenyl radicals with the limitation that a total of not less than about 3 and not more than about 6 p-hydroxy phenyl groups can be present in the compound; and *n* is a number having an average value from 1 to about 6.

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 monomer.

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. The treated article of claim 1, wherein said dye-resisting agent is 1,1,2,2-tetrakis 4-hydroxyphenyl ethane.

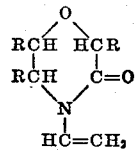
18. The treated article of claim 1, wherein said dye-resisting agent is tris(p-hydroxyphenyl)methane.

19. The treated article of claim 1, wherein said dye-resisting agent is 1,1,2,2-tetrakis-p-hydroxy-phenyl propane.

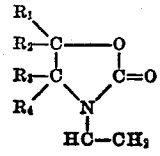
20. The treated article of claim 1, wherein said dye-resisting agent is 1,1,2,2-tetrakis-p-hydroxy-phenyl-pentane.

21. The treated article of claim 1, wherein said dye-resisting agent is 1,1,2,2-tetrakis-p-hydroxy-phenyl-hexane.

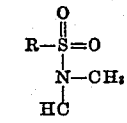
22. Treatment for a synthetic fiber to reduce its receptivity to dyestuffs, said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essentially of (A1) between about 80 and about 99 weight percent, based on dry fiber weight, of a fiber-forming acrylonitrile addition polymer with (A2) between about 20 and about 1 weight percent, based on dry fiber weight, of an azotic 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 (A2*a*) N-vinyl lactam monomers; (A2*b*) 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; (A2*c*) 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; (A2*d*) N-vinyl-N-methyl-alkylsulfonamide 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 (A2*e*) 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, based on the weight of graft copolymerized substituent, of (B2*a*) N-vinyl lactam monomers; (B2*b*) said N-vinyl-3-morpholinone monomers; (B2*c*) said N-vinyl-2-oxazolidinone monomers; (B2*d*) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (B2*e*) 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 (C2*a*) N-vinyl lactam monomers; (C2*b*) said N-vinyl-3-morpholinone monomers (C2*c*) said N-vinyl-2-oxazolidinone monomers; (C2*d*) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (C2*e*) 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 a dye-resisting agent effective against direct and acid dyestuffs as defined by Formula I in claim 1.

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