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ACRYLONITRILE COPOLYMERS, BLENDS AND GRAFTS MADE DYE RESISTANT WITH HYDRO-CARBON SUBSTITUTED PHENOLS

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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 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 strain-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

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alloy" fibers when they are dyed in the presence of other fibers, such as cellulose 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 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.

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-vinyl caprolactam) or polymerized N-vinyl-2-oxazolidinone (including especially the unsubstituted and methyl and ethyl ring substituted species) or polymerized N-vinyl-3-morpholinones (especially N-vinyl-3-morpholinone) constituents as dye-receptive adjuvants for the fibers, 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 article constructed therefrom, having their degree of dye-receptivity or susceptibility to coloration of straining 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.

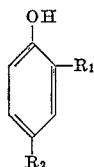
Still an additional object of the invention is to furnish a method or means for controlling the dye-receptivity of

"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 possibilitate 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 direct level dyeing acid, mordant, and acid premetallized 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 agents of the present invention in the accomplishment of the intended purpose.

A further object of the invention is to provide "nitrile alloy" fibers that are in a form suitable to have their dye receptivity altered over a varying range of coloration to have increased fastness to light when dyed with direct and acid premetallized dyestuffs and treated with the reserving agents of the present invention.

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 compound or mixtures of compounds represented by the general structure:



(I)

wherein R_1 and R_2 are 1 to 12 carbon atom radicals or hydrogen, the sum of the carbon atoms of R_1 and R_2 is at least 4 and up to about 12, and one of R_1 and R_2 is at least a 4-carbon atom radical. Some representative compounds that fall within this structure and which are useful as reserving agents in this invention are: ortho- and para-tertiary-amyphenol (OTAP and PTAP, respectively), ortho- and para-cyclohexylphenol (OCHP and PCHP), ortho- and para-tertiary-octylphenol (OTOP and PTOP), ortho- and para-phenylphenol, ortho- and para-benzylphenol, 2-methyl-4-tertiary-octylphenol, 2,4-di-tertiary-butylphenol, etc. It has been found that when R is an alkyl radical, the tertiary configuration is superior to the secondary configuration which is superior to the primary configuration. 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 8 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 8 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 cellulose 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 types of dyestuffs when used to dye cellulosic blends of the "nitrile alloy" fibers and certain acid premetallized 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 effect or influence on the physical or aesthetic characteristics and properties of the fibers on which they are applied except when quantities in excess of about 20 percent on the fiber are used, which tends to cause a stiffening of the fiber. 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.

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 "nitrile alloy" 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 application formulation is relatively immaterial. 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 10 percent of the dye-resisting agent, based on the weight of the dry "nitrile alloy" fiber (OWF) and depending on the type of dyeing procedure used. Suitable application of the resisting agent may be made when the liquor-to-fiber ratio of the applying formulation to the total 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 20:1 to 30:1, respectively.

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Various techniques may be utilized for preparing suitable applying formulations of the dye reserving or resisting agent. The water solubilities of the phenols represented by Formula I range from very slightly soluble to insoluble. Thus, as is apparent, for most of these phenols, emulsion application to the fibers is most advantageous and frequently necessary. Such emulsions may be prepared by adding the reserving agent and an emulsifier to a predetermined amount of water and mixing with a suitable mixer. It is desirable that the emulsion be stable in the range from about 40° C. to 100° C. in concentrations of 0.1 to about 20 percent of the reserving agent based on the weight of the "nitrile alloy" fiber. Several emulsifying agents have been found that will satisfy these requirements, particularly Aerosol OT (sodium dioctylsulfosuccinate, supplied by the American Cyanamid Company), Monawet MO (70% di (2 ethylhexyl) sodium sulfosuccinate, 12% butyl carbitol, 17% water, 1% unlisted, supplied by Mona Industries, Incorporated) and Alrowet D65 (65% sodium dioctylsulfosuccinate and an unlisted wetting agent, supplied by Geigy Industrial Chemicals). Usually, between about 20 and 50 percent, based on the weight of the reserving agent, of the emulsifying agent is required to produce the emulsions falling within the above limits. As stated before, the completeness and levelness of reservation is quite dependent on the concentration of reserving agent used; however, it is also somewhat dependent on the temperature of emulsion preparation and pretreatment. Generally, for complete reservation of direct level dyeing acid, mordant, and acid premetalized dyes, optimum results are obtained with at least an 8-10 percent, on the weight of the "nitrile alloy" fiber, concentration of the reserving agent and an emulsion preparation at or near the melting point of the reserving agent. Less than complete reservation can be obtained with lower concentrations.

A typical treatment of the fibers involves pretreating a scoured blend of a "nitrile alloy" fiber and cotton in an aqueous emulsion of 10 percent, on the weight of "nitrile alloy" fiber (OWF) of a reserving agent of (I) or mixtures of these reserving agents and 3 percent (OWF) of an emulsifier for twenty minutes at 80-90° C. The emulsion is prepared by beating the reserving agent and emulsifier into that volume of about 90° C. water required to make a 30:1, on the weight of the fiber blend (OWB), liquor-to-fiber ratio pretreatment bath. The Brookfield Counter Rotating mixer is very useful for this emulsion preparation, but may in some cases be replaced by the use of a small amount of solvent. The exhausted pretreatment bath is cooled to about 60° C., and 0.5 percent, on the weight of the cotton (OWC), of a direct dyestuffs is added and typical dyeing techniques are used to complete the dyeing of the fiber. Procedures such as the above will usually produce a dyed fiber blend in which the cotton is deeply dyed and the "nitrile alloy" fiber is left white or essentially white. 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 reserving agent prior to dyeing, the applying formulation may be prepared and used for deposition of the reserving 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 and the particular reagents in the dyebath.

In addition, somewhat in the manner of conventional textile finish application, the dye resisting agent may be

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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 treatment or treatments in a conventional dye beck.

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 5-gram sample of a "nitrile alloy" fiber comprised of polyacrylonitrile containing uniformly incorporated therein, as a dye-assisting adjuvant, about 8 percent on the weight of the fiber (OWF) of poly-N-vinyl pyrrolidone having a Fikentscher K-value of about 55, and a 5-gram sample of cotton, both in fabric form and scoured, were pretreated in an aqueous emulsion of 10% (OWF) of p-tert-octylphenol and 3% (OWF) of Aerosol OT (dioctyl sulfosuccinate). The emulsion was prepared by beating the phenol and Aerosol OT into that volume of water required to make a 30:1 liquor to total fiber ratio. Exhaustion of the phenol was complete after about 15 minutes at 90° C. The exhausted pretreatment bath was cooled back to 60° C. and 0.5% (OWC) of Diphenyl Brilliant Blue FF (C.I. Direct Blue 1) was added. The temperature was raised to 80° C. in 10 minutes and maintained at that temperature for two hours. Dye exhaustion with 10% (OWC) common salt followed 30 minutes after reaching 80° C.; another 10% OWC salt was added ten minutes later. The fiber samples, after dyeing, were removed from the dye bath, rinsed and dried. The "nitrile alloy" fiber was completely reserved, or left white, while the cotton was dyed a medium blue.

EXAMPLE 2

When the procedure of Example 1 was used except to leave out the p-tert-octyl phenol, the "nitrile alloy" fiber sample was dyed a medium blue and the cotton was dyed a light blue.

EXAMPLE 3

The same procedure of Example 1 was repeated except to use o-cyclohexylphenol in place of the p-tert-octylphenol, wool in place of the cotton, and Gycolan Blue (Acid Blue 158) in place of the Diphenyl Brilliant Blue FF. Dyeing was for two hours at 95° C. with exhaustion by 2%, on the weight of the wool (OWW), of sulfuric acid. The "nitrile alloy" fiber was completely reserved while the wool dyed a medium blue.

EXAMPLE 4

When the procedure of Example 3 was used except to leave out the o-cyclohexylphenol, the "nitrile alloy" fiber was dyed a light blue and the wool was dyed a light-medium blue.

EXAMPLE 5

When the procedures of Examples 1 and 3 were repeated except to omit the emulsifying agent, reservation of the "nitrile alloy" fiber was incomplete and extremely uneven and unacceptable.

EXAMPLE 6

The results of other experiments carried out according to the procedures of Examples 1 and 3 are shown in Table 1.

minutes at 45° C., raised slowly to the boil and run for 30 minutes. 2% (OWW) sulfuric acid was added and the dyeing continued for another 2 hours after which the bath was cooled to 70° C. 2% (OWW) sodium dichromate was added, the bath slowly raised to the boil

Table 1

Dye	Dye Class	Color Index	Blend	Reserv. Agent	Pehmol, Percent OWF	Dye, Percent OWC(w)	Aerosol OT, Percent OWF	Reservation of "Nitrile Alloy"
Diphenyl Brilliant Blue FF.	Direct	Direct Blue 1	"Nitrile Alloy" Cotton (50-50).	PTOP	5.0	0.5	1.5	Moderate.
Do.	do.	do.	do.	PCHP	10.0	0.5	3.0	Complete.
Do.	do.	do.	do.	PCHP	5.0	0.5	1.5	Moderate.
Fastul Blue LFGL	Acid Pre-met.	Direct Blue 99	do.	PTOP	10.0	0.5	3.0	Complete.
Gycolan Blue GGL	do.	Acid Blue 158	"Nitrile Alloy" Wool (50-50).	PTOP	10.0	0.5	3.0	Do.
Do.	do.	do.	do.	PTOP	5.0	0.5	1.5	Moderate.
Do.	do.	do.	do.	PCHP	10.0	0.5	3.0	Complete.
Do.	do.	do.	do.	PCHP	5.0	0.5	1.5	Moderate.
Do.	do.	do.	do.	PTAP	10.0	0.5	3.0	Complete.
Gycolan Green BFL	do.	Acid Green 12	do.	PTOP	10.0	0.5	3.0	Do.
Palatine Fast Black	do.	Acid Black 52	do.	PTOP	20.0	5.0	6.0	Moderate. ²
WANA					10.0	6.0	3.0	Slight.

¹ "Nitrile Alloy" separately pretreated. ² "Nitrile Alloy" stiff.

EXAMPLE 7

When the procedures of Example 1 is repeated except in substitute viscose rayon yarn for the cotton, similar excellent results are obtained.

EXAMPLE 8

When the procedures of the foregoing examples were duplicated, excepting to employ (in place of the therein utilized "nitrile alloy" fibers) fibers containing about 7 percent (OWF) of poly-N-vinyl-3-morpholine incorporated as the dye-assisting adjuvant in place of the PVP in the "nitrile alloy" fibers, similar excellent results were achieved.

EXAMPLE 9

When the procedures of the foregoing examples are duplicated, excepting to employ (in place of the therein utilized "nitrile alloy" fibers) fibers containing either poly-N-vinyl caprolactam, or poly-N-vinyl-2-oxazolidinone as the dye-assisting adjuvant in place of the PVP or PVM 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 are also achieved when the resisting agents are applied on blends of the fibers of the foregoing. 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, feather-keratein, casein fibers, protein fibers and the like proteinous or so called Azlon fibers of natural, artificial, regenerated, or reconstituted origin.

EXAMPLE 10

An aqueous 20:1 liquor to total fiber emulsion was prepared at 80° C. with 10%, on the weight of the "nitrile alloy" fiber (OWF), para-tertiary-octyl-phenol and 3% (OWF) Aerosol OT. The emulsion was cooled at 45° C. and a 10 gram fiber blend consisting of 5 grams of polyacrylonitrile containing about 7% PVP and 5 grams of wool was treated in the emulsion for 1 hour. The liquor ratio was raised to 50:1 and 5% (OWW) Omega Chrome Black 2G (C. I. Mordant Black 26), a mordant dye, 0.5% (OWW) Palatine Fast Salt O (no C. I.), and 3% (OWW) formic acid. The dyeing was run for 10

and run for 30 minutes. The sample was rinsed and dried. The wool was dyed a deep black but the PVP-containing PVCN fibers were left almost completely white.

Without the use of the para-tertiary-octyl-phenol reserving agent, the wool dyed a full black and the PVP-containing PVCN fibers dyed a medium grey-violet.

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 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 mono-

mers, 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-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 a minor proportion of any of the polymer products from the specified azotic monomers or mixtures thereof, primarily as dye-assisting adjuvants.

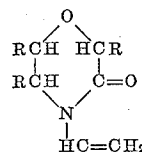
Such species of "nitrile alloy" fibers are capable of being accurately described as synergetic and anisotropic clathrates that are composed of a hydrophilic polymer. In such varieties of the "nitrile alloy" fibers (as well as in other of the forms in which they may be obtained) there is a mutually enhancing 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 Textile 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 secured 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-alkyl-sulfonamide 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 component monomers to be present as the beneficial component in "nitrile alloy" fibers in a amount that is in the neighborhood or range of from about 5 to 15 percent by 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-pyrrolidinone 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

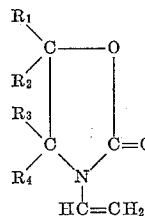
N-vinyl-N-methylmethylsulfonamide; as the polymeric adjuvant that is blended with the essential acrylonitrile polymer base in the "nitrile alloy" composition. When physically blended "nitrile alloy" products are prepared that utilize, as the beneficial additament or constituent, copolymeric or graft 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 somewhat related products derived in any of the ways described from N-vinyl-3-morpholinones of the structure:



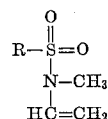
wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon alkyl radicals, 6 to 10 carbon aryl radicals and equivalents thereof.

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 alloy" include those represented by the formula:

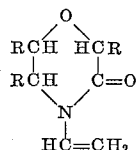


where R is hydrogen, a 1 to about 4 carbon alkyl radical, a 6 to about 10 carbon aryl radical or some equivalent thereof.

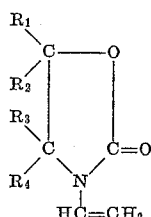
Suitable "nitrile alloy" products may also be manufactured from other beneficial additaments or components that are more or less equivalent to those derived from the azotic monomers indicated in the foregoing. Thus, other varieties of N-heterocyclic monomers more or less similar or related to the specified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

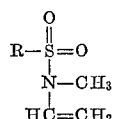
1. A synthetic textile fiber which is characterized in having its normal receptivity to dyestuffs modified so as to have dye-resisting characteristics, said fiber being a member selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends consisting essentially of (A1) 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 to about 1 weight percent, based on dry fiber weight, of an azotic polymeric dye-assisting adjuvant selected from the group consisting of additional 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 4 carbon atom alkyl substituents and 6 to 10 carbon atom aryl substituents; (A2c) N-vinyl-2-oxazolidinone monomers of the structure:

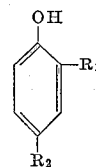


in which R₁, R₂, R₃ and R₄ are independently selected from the group consisting of hydrogen, 1 to 4 carbon atom alkyl substituents and 6 to 10 carbon atom aryl substituents; (A2d) N-vinyl-N-methyl-alkylsulfonamide monomers of the structure:



wherein R is selected from the group consisting of hydrogen, 1 to 4 carbon atom alkyl substituents and 6 to 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 preformed 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 (B2a) N-vinyl lactam monomers; (B2b) said N-vinyl-3-morpholinone monomers; (B2c) said N-vinyl-2-oxazolidinone monomers; and (B2d) said N-vinyl-N-methyl-alkylsulfonamide monomers; and (B2e) mixtures thereof; and (C) fiber-forming graft copolymers consisting 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, level dyeing acid, mordant, and acid pre-metallized dyestuffs between about 0.1 and 20 percent by weight, based on the weight of the fiber, of a compound represented by the structure:



(I)

wherein R₁ and R₂ are independently selected from the group consisting of 1 to 12 carbon atom alkyl radicals, 6 to 10 carbon atom cycloalkyl radicals, 6 to 10 carbon atom hydrocarbon aryl radicals, and hydrogen, and wherein the sum of the carbon atoms of R₁ and R₂ is at least 4 and up to 12, and when R₁ and R₂ are both alkyl radicals at least one of R₁ and R₂ is at least a 4 carbon atom radical.

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 8 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 8 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 a 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.

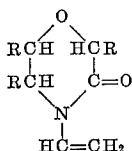
15. The treated fiber of claim 1, wherein said synthetic fiber consists of an intimate polymer blend of polyacrylonitrile and poly-N-vinyl-2-oxazolidinone as a dye-assisting adjuvant.

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

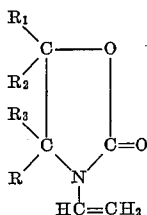
17. Treatment for a synthetic fiber to reduce its receptivity to direct, level dyeing acid, mordant, and acid premetallize dyestuffs, said fiber being selected from the

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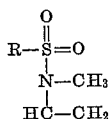
class of synthetic textile fibers consisting of (A) intimate polymer blends consisting essentially of (A1) between about 80 and about 99 weight percent, based on dry fiber weight, of a fiber-forming acrylonitrile addition polymer with (A2) between about 20 and about 1 weight percent, based on dry fiber 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 (A2a) N-vinyl lactam monomers; (A2b) N-vinyl-3-morpholinone monomers of the structure:



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



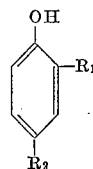
in which R₁, R₂, R₃, and R₄ are independently selected from the group consisting of hydrogen, 1 to 4 carbon atom alkyl substituents and 6 to 10 carbon atom aryl substituents; (A2d) N - vinyl - N - methyl - alkylsulfonamide monomers of the structure:



wherein R is selected from the group consisting of hydrogen, 1 to 4 carbon atom alkyl substituents and 6 to 10 carbon atom aryl substituents; and (A2e) mixtures thereof; (B) fiber-forming graft copolymers consisting 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 (B2a)

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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 consisting 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; (C2d) said N - vinyl - N - methyl - alkylsulfonamide monomers; and (C2e) mixtures thereof, which treatment comprises impregnating the fiber with between about 0.1 and 20 percent by weight on the weight of the fiber of a compound represented by the structure:



wherein R₁ and R₂ are independently selected from the group consisting of 1 to 12 carbon atom alkyl radicals, 6 to 10 carbon atom cycloalkyl radicals, 6 to 10 carbon atom hydrocarbon aryl radicals, and hydrogen, and wherein the sum of the carbon atoms of R₁ and R₂ is at least 4 and up to 12, and when R₁ and R₂ are both alkyl radicals at least one of R₁ and R₂ is at least a 4 carbon atom radical.

18. The treatment of claim 17 wherein the compounds of (I) are applied from an aqueous emulsion.

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Examiners.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,206,272

September 14, 1965

Robert F. Johnson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 58, for "of straining" read -- or staining --; column 4, line 37, for "'balacing'" read -- "balancing" --; line 48, for "fiibers" read -- fibers --; line 58, for "application" read -- applicating --; column 11, line 12, for "additional" read -- addition --.

Signed and sealed this 2nd day of August 1966.

EAL)

test:

ARNEST W. SWIDER

Testing Officer

EDWARD J. BRENNER

Commissioner of Patents