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POLYPHENOLIC POLYMER RESERVING AGENTS 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 integral proportions of either, or both, various N-vinyl lactam polymers and copolymers or derivatives thereof; N-vinyl-2-oxazolidinone polymers or 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 or wool and other proteinous fibers (both natural and artificial or synthetic in origin) with which the "nitrile alloy" fibers may be blended as

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well as that of achieving union dyeing or uniform color level in such blends 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 in the same or sequential 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-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 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 or degree of control desired, of a certain variety of polyphenolic polymer or condensate, 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" 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 cellulosic 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 or after-treated direct types of dyestuffs when used to dye cellulosic blends of the "nitrile alloy" fibers and certain acid dyestuffs with proteinous blends. In any case, the precise quantity of the reserving agent that is necessary to be applied 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. In general, dye reserving or resisting agents have no excessive deleterious effect or intolerable influence on the physical or 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 impunity in this regard. Of course, as might be anticipated, certain specific effects and properties (such as hand, light stability, chlorine resistance, etc.) may be found to vary within reasonable limits depending upon the quantity and particular species of treating agent employed. 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 achiev-

ing excellent results in restraining the action of direct and certain acid dyes on "nitrile alloy" fibers.

The polyphenolic polymer reserving agents that are so advantageously employed in combination with the "nitrile alloy" fibers in the practice of the present invention may be characterized as being low molecular weight polymers that contain a high proportion of phenolic hydroxy groups to phenyl units in their molecules and wherein each hydroxy group is unhampered by steric hindrance, especially by groups in the ortho position of the phenolic rings. The maximum size of the polyphenolic polymers that may be employed is limited by their solubility characteristics. The polyphenolic polymer reserving agents must be soluble at any practical or desired temperature (generally room temperature) in aqueous sodium hydroxide solution having a concentration of NaOH between about 1 and 20 percent by weight or in low molecular weight aliphatic alcohols, including methanol, ethanol or isopropanol, or in lower aliphatic ketones such as acetone or methyl ethyl ketones, or in both types of water dilutable solvent vehicles. The polyphenolic polymer reserving agents must also be capable of remaining either in solution or have the capacity of being solubilized with suitable dispersing agents, or to remain in finely divided emulsion, dispersion, or stable suspension, upon extreme dilution of their caustic or alcoholic preparatory solutions with water, such as extreme dilutions of up to 1000 times. In some instances, the initially prepared formulation may not require further dilution.

The caustic soluble polyphenolic polymer reserving agents are comprised of, or consist of, molecules containing a plurality of aromatic nuclei derived from such phenolic monomers as are selected from the group consisting of phenol, Bisphenol-A (p,p'-isopropylidene diphenol), Bisphenol-B (p,p'-sec.-butylidene diphenol), bisphenol sulfone (p,p'-sulfonyldiphenol), bisphenol sulfoxide (p,p'-sulfinyldiphenol) and mixtures thereof that are condensed or linked together by about equimolar quantities of bridging agents selected from the group consisting of methylene, ethylene, and ethylidene radicals, isopropylene radicals, bivalent radicals from divinyl benzene, bivalent radicals from isopropenyl phenols, and mixtures thereof. Alternatively, and with equal advantage, certain of the polyphenolic polymer reserving agents within the scope of the invention can be provided by using such double functional monomers as vinyl or isopropenyl phenols to obtain products of self-reaction.

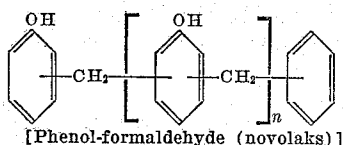
The linkages in the aromatic nuclei of the polyphenolic polymers (such as the methylene linkages to phenol rings) may be either ortho or para, or both ortho, with respect to the phenyl hydroxy group attached to the aromatic nucleus. As indicated, the linkages between the condensed or polymerized phenolic monomer units may be of mixed sorts in the finally obtained polymer chain. Bisphenol monomers that are linked together to form the polyphenolic polymer reserving agents may be linked in the polymer structure from the same phenyl group, or they may have individual links or bridging units attached to separate phenyl groups in the linked aromatic nucleus. Vinyl and isopropenyl derived linkages may have either one or two carbons between linked aromatic nuclei, each with or without side chains. While the polyphenolic polymer reserving agents must have the above indicated solubility characteristics and the herein-after defined arrangement of hydroxyl groups per interconnected aromatic nucleus in their structure, such characteristics cannot positively and absolutely be correlated or limited by maximum molecular weights of the diverse varieties of polyphenolic polymers that may be employed. In general, the molecular weight of the polyphenolic polymer reserving agent must be at least about 300. However, it may be as high as 2000 or more. An advantageous range of molecular weight for the polyphenolic polymers that are utilized is between about 400 and

1000. The polymers are insoluble in water but soluble in dilute alkali, alcohols, ketones and most other polar solvents.

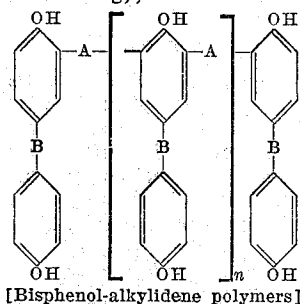
Ordinarily, optimum results and greatest advantages are achieved for the polyphenolic polymer reserving agents when they contain about one phenolic hydroxyl unit per single phenyl group or other aromatic nucleus in their structure. In polyphenolic polymers that have less than one hydroxyl group per single phenyl group, it is desirable for a high ratio of hydroxyl groups to interconnected aromatic nuclei to be obtained in the polymer, such as a ratio of at least about 0.5 and up to 2.0 but preferably about 1.0 phenolic hydroxyl groups per aromatic nucleus or phenyl ring in the structure. As is apparent, it is necessary for the polyphenolic polymers to contain hydroxyl groups on conjugated ring systems. Alkoxy substituents on phenyl groups are not operative nor do they provide the desired capabilities for the reserving agents used in the practice of the present invention. Neither are hydroxy cyclohexyl or the like units.

As mentioned, at least one ring position ortho to the phenyl hydroxyl must be left unoccupied in the polyphenolic polymer reserving agents. The dye-resisting activity of polyphenolic polymers having substitutions ortho to the phenolic hydroxyl units is generally found to be decreased to an undesirable, and not reliably useful, extent. Polyphenolic polymers of the same general type as above described which have double ortho substitutions adjacent to the phenolic hydroxyl units ordinarily are found to be entirely hindered for purposes of the present invention. Their activity with respect to their capability of resisting the action dyestuffs and coloring agents is found to be completely suppressed.

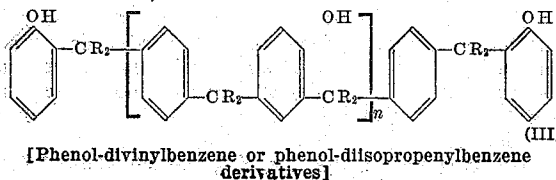
While they are neither comprehensive nor intended to depict all possibilities, the following structural formulae are illustrative of general types of polyphenolic polymer structures that may be utilized with great advantage as dye-resisting agents in the practice of the present invention.



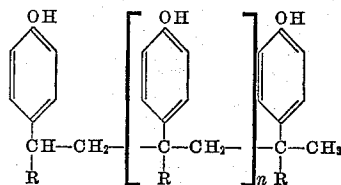
wherein n is an integer having an average value of one or more (and either ortho- or para-attachments, or both, may be present in the ring);



wherein A is a bridging or linking unit selected from the group consisting of methylene ($-\text{CH}_2-$), ethylene ($-\text{CH}_2\text{CH}_2-$), ethylidene ($-\text{CHCH}_3-$), isopropylidene ($-\text{CH}(\text{CH}_3)_2-$), and the like; B is isopropylidene ($-\text{C}(\text{CH}_3)_2-$), sulfonyl ($-\text{SO}_2-$), sulfinyl ($-\text{SO}-$) and the like; and n has a value of 0 or some positive numerical value;



wherein each R is independently selected from the group consisting of hydrogen and methyl radicals with the limitation that not more than one R in any linkage may be hydrogen, and n has a value of 0 or some positive numerical value; and



[Vinyl phenol or isopropenyl phenol homopolymers]

15 wherein R is selected from the group consisting of hydrogen or methyl radicals and n has a value of 0 or some positive numerical value.

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. 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 used and depending upon the type of dyeing procedure. 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 1 and 100 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 2:1 to 50:1, respectively.

Various techniques may be utilized for preparing suitable applying 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 caustic or 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 agents may be added to dyed fibers in intermediate stages or after completion of dyeing by incorporating 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 applying formulations by distributing the formulation directly to a running

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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 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 a dye-resisting agent consisting of a common novolak resin having an average molecular weight of about 800 and an average of about 7.5 formaldehyde linked phenol units per molecule. 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 a Fikentscher K-value of about 55. The viscose rayon yarn was a dull yarn having a staple length of about 1½ inches and a denier of about 3. The dye-resisting agent was applied to the blended fiber mixture after first dissolving 5 parts of the novolak resin in about 1.6 parts of sodium hydroxide and 20 parts of water, 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, diluted solution of the novolak resin for 20 minutes at 70° C. Without removing the fiber blend from the applying solution of the resisting agent, about one part of Fastusol Blue L7GA (Prototype No. 432), 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 71° 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 while 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 types of fibers in the blend was obtained.

Example 2

The procedure of Example 1 was repeated, excepting to substitute for the novolak resin an analogous Bisphenol-A-formaldehyde resin having an average molecular weight of about 500 as the polyphenolic polymer dye-reserving agent. Identical results were obtained.

Example 3

The procedure of Example 1 was again repeated, excepting to employ as the reserving agent a Bisphenol-A diisopropenyl benzene polyphenolic polymer having an average molecular weight of about 1000. Identical results were obtained.

Example 4

The procedure of the first example was repeated, excepting to employ as a resisting agent a condensation

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product of Bisphenol-A with divinyl benzene having an average molecular weight of about 1000. Identical results were obtained.

Example 5

A fabric constructed from yarn that was composed of a blend, in equal weight proportions, of middling cotton staple with a "nitrile alloy" staple fiber similar to that used in the first example was dyed in the conventional manner with about 0.5 percent Cibalan Black BGL (no Color Index). The "nitrile alloy" component of the blended yarn in the fabric was observed to be dyed to a gray coloration, while the cotton remained white. Following the initial dyeing, and using the same bath, about 4 percent o.w.f. of the same polyphenolic polymer reserving agent as employed in the second example, along with enough sodium hydroxide to solubilize the reserving agent, was added to the liquor. The liquid medium was circulated through the fabric for about 10 minutes. After this application of the reserving agent, about 1 percent o.w.f. of Diphenyl Red 4B Supra (Color Index 448) was added to the bath and run at 80° C., with the addition of 10 percent o.w.f. of sodium chloride over a one hour period. A two-tone effect was obtained in the fabric, with the "nitrile alloy" constituent having the initial gray color and the cotton being red. In contrast, when the foregoing was repeated excepting to eliminate the application of dye-resisting agent between the dyeings, the fabric came out with all of the diverse fiber components therein dyed to a red shade of coloration.

Example 6

The procedure of Example 5 was repeated, excepting to employ the polyphenolic polymer described in Example 1 as the dye-resisting agent. Identical results were obtained.

Example 7

The procedure of Example 5 was repeated, excepting to employ the polyphenolic polymer described in Example 3 as the dye-resisting agent. Identical results were obtained.

Example 8

The procedures of each of the seven preceding examples were repeated excepting to use a "nitrile alloy" fiber in the blend that was comprised of polyacrylonitrile containing poly-N-vinylcaprolactam as the dye-assisting adjuvant in place of the PVP. Identical results were achieved.

Example 9

The procedures of each of the first seven examples were again duplicated, excepting to use as the "nitrile alloy" a fiber that had been prepared from an analogous polymer blend of polyacrylonitrile with poly-N-vinyl-2-oxazolidinone having a Fikentscher K-value of about 13 being substituted for the PVP as the dye-assisting adjuvant. Identical results were obtained.

Example 10

The procedures of each of the first seven examples are again duplicated excepting to employ a "nitrile alloy" fiber in the blend that is comprised of polyacrylonitrile containing poly-N-vinyl-5-methyl-2-oxazolidinone (K-29) instead of the PVP as a dye-assisting adjuvant. Identical results are obtained.

Example 11

The procedures of each of the first examples are again duplicated, excepting to employ a "nitrile alloy" fiber in the blend that is comprised of polyacrylonitrile containing poly-N-vinyl-3-morpholinone (K-60) instead of the PVP as a dye-assisting adjuvant. Identical results are obtained.

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 polymer 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 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 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 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-alkyl-sulfonamides. Thus, the "nitrile alloy" may be comprised of the acrylonitrile poly-

mer 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.

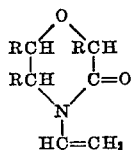
Such species of "nitrile alloy" fibers are capable of being accurately described as synergetic and anisotropic clathrates that are composed of a hydrophobic polymer in combination with a hydrophilic polymer. In such varieties of the "nitrile alloy" fibers (as well as in other of the forms in which they 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 a 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 homopolymer N-vinyl-methylalkylsulfonamide polymer such as homopolymeric N-vinyl-N-methyl-sulfonamide; as the polymeric adjuvant that is blended with the essential acrylonitrile polymer base in the "nitrile

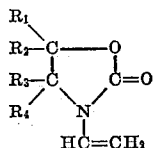
alloy" composition. When physically blended "nitrile alloy" products are prepared that utilize, as the beneficial additament or constituent, copolymeric or graft copolymeric products of the indicated azotic monomers, it is usually beneficial for the polymeric adjuvants that are employed to be those which 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:



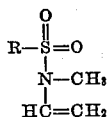
wherein each substituent R unit is independently selected from the group consisting of hydrogen, 1 to about 4 carbon alkyl radicals, 6 to about 10 carbon aryl radicals and equivalents thereof.

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 the 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:

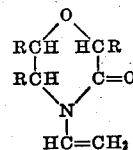


wherein R is hydrogen, a 1 to about 4 carbon alkyl radical, a 6 to about 10 carbon aryl radical or some equivalent thereof.

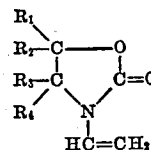
Suitable "nitrile alloy" products may also be manufactured from other beneficial additaments or components that are more or less equivalent to those derived from the azotic monomers indicated in the foregoing. Thus, other varieties of N-heterocyclic monomers more or less similar or related to the specified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

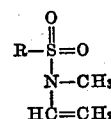
1. A synthetic textile fiber which is characterized in having its normal receptivity to dyestuffs modified so as to have dye-resisting characteristics, said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essentially of (A1) between 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 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 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-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 (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, 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 and acid dyestuffs between about 0.1 and 20 percent by weight, based on the weight of the fiber, of a compound that is a poly-

phenolic condensation polymer containing phenolic units selected from the group consisting of phenol, p,p'-isopropylidene diphenol, p,p'-sec-butylidene diphenol, bisphenol sulfone, bisphenol sulfoxide, and mixtures thereof that are linked with less than equimolar quantities of bridging agents selected from the group consisting of methylene radicals, ethylene radicals, ethylidene radicals, isopropylene radicals, bivalent radicals from divinyl benzene, bivalent radicals from isopropenyl phenols, and mixtures thereof; said polyphenolic polymer having a molecular weight of between about 300 and about 2000 and being soluble in lower alkyl alcohols and aqueous sodium hydroxide solutions having concentrations of sodium hydroxide of from about 1 to 20 percent by weight; said polyphenolic polymers containing between about 0.5 and 2 phenolic hydroxyl unit per phenyl unit in their molecules.

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 a phenol-formaldehyde novolak of 4.0-8.0 phenol units per polymer molecule.

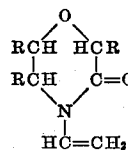
18. The treated article of claim 1, wherein said dye-resisting agent is a Bisphenol-A formaldehyde novolak containing about 2.0-4.0 p,p'-isopropylidene diphenol units per polymer molecule.

19. The treated article of claim 1, wherein said dye-resisting agent is a homopolymer of isopropenylphenol.

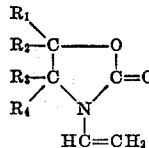
20. The treated article of claim 1, wherein said dye-resisting agent is a condensation product of p,p'-isopropylidene diphenol with divinyl benzene.

21. The treated article of claim 1, wherein said dye-resisting agent is a condensation product of p,p'-isopropylidene diphenol with diisopropenyl benzene.

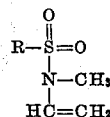
22. Treatment for a synthetic fiber to reduce its receptivity to dyestuffs; said fiber being selected from the class of synthetic textile fibers consisting of (A) intimate polymer blends comprised essentially of (A1) between about 80 and about 99 weight percent, based on dry fiber weight, of a fiber-forming 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 (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 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; (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)

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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 a dye-resisting agent effective against direct and acid dyestuffs that is a compound that is a polyphenolic condensation polymer containing phenolic units selected from the group consisting of phenol, p,p'-isopropylidene diphenol, p,p'-sec-butylidene diphenol, bisphenol sulfone, bisphenol sulfoxide, and mixtures thereof that are linked with less than equimolar quantities of bridging agents selected from the group consisting of methylene radicals, ethylene radicals, ethylidene radicals, isopropylene radicals, bivalent radicals from divinyl benzene, bivalent radicals from isopropenyl phenols, and mixtures thereof; said polyphenolic polymer having a molecular weight of between about 300 and

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about 2000 and being soluble in lower alkyl alcohols and aqueous sodium hydroxide solutions having concentrations of sodium hydroxide of from about 1 and 20 percent by weight; said polyphenolic polymers containing between about 0.5 and 2 phenolic hydroxyl unit per phenyl unit in their molecules.

References Cited in the file of this patent

UNITED STATES PATENTS

2,623,806 Fuchs Dec. 30, 1952

FOREIGN PATENTS

759,595 Great Britain Oct. 24, 1956

OTHER REFERENCES

Sandoz: J.S.D.C., vol. 66, October 1950, p. 564.