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FIBROUS TEXTILE AND INDUSTRIAL FABRICS

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The present invention is concerned with the production of fabrics formed of mechanically interlocked fibers, filaments, yarns and/or threads.

It is an object of the present invention to provide novel and improved fabrics for textile and industrial uses comprising fibers having ion-exchange groups. One object is to provide fabrics comprising this type of fiber or filament which is characterized by resistance to the development of static electricity by rubbing or other mechanical action. Another object of the invention is to provide fabrics comprising this type of fiber having desirable dyeing and moisture regain qualities. Another object of the invention is to provide fabrics of this type of fiber which are characterized by both good tenacity and toughness. Another object of the invention is to provide fabrics which are adapted to be used as ion-exchange media and which in such use do not undergo excessive swelling in aqueous media. Another object of the invention is to provide fabrics of the various types stated which have outstanding durability under normal conditions of usage including not only normal textile wear, but also such industrial usage as requires repeated subjection to aqueous liquids with or without intervening drying. These objects and other advantages of the invention will be apparent from the description thereof hereinafter.

The fabrics of the present invention comprise fibers formed of amine-containing polymers which are cross-linked by a poly- or di-functional alkylating agent. The polymeric material of which the fibers are formed may be in cross-linked condition at the time the fibers are converted into fabrics, as by weaving, knitting, carding, or the like. Alternatively, aminolyzable polymers containing no amine groups or un-cross-linked linear polymers containing amine groups may be converted into the desired type of fabric after which the latter type of fiber is cross-linked by treatment of the fabric with a difunctional alkylating agent or the former type of fiber is aminolyzed to introduce amine groups into the polymer of which it is formed and then the fabric is treated with the difunctional alkylating agent to effect cross-linking of the polymer making up the fibers.

In accordance with the present invention, any of the fibers just described are assembled or fabricated into various types of fabrics including those involving interlocked yarns or threads formed of plied yarns and those of felt-like character in which the fibers or filaments are interlaced or interlocked with or without being adhesively bonded at their points of intersection or interlocking. The former type of fabric may be a woven, knitted, netted, knotted, or braided fabric formed of yarns comprising fibers or filaments of the type specified. Fabrics contemplated by the present invention are also obtainable by the haphazard distribution of a multiplicity of fibers either of short lengths or of continuous length. This includes such fabrics as are obtained by carding, and if desired, superimposing a plurality of carded webs upon one another with the machine direction of the various webs disposed either parallel to one another or at various angles for the purpose of providing either anisotropy or isotropy in the characteristics of the resulting fabric, particularly as to strength and cleavage. Intermediate forms, which may also be termed hybrid forms, of fabrics may be involved such as the type of fabric known as needle felts wherein

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a woven or knitted fabric has fibers or filaments punched through the woven base fabric.

The various fabrics may be formed entirely of fibers, filaments, and yarns of the type defined above or they may comprise a blend of fibers or filaments of this type with fibers or filaments of other types, either natural or artificial in origin. Similarly, the fabrics may be formed of a mixture of yarns comprising fibers or filaments of the type defined above with yarns formed of other fibers, either natural or artificial. Thus, the fabrics may also comprise fibers, filaments, or yarns of cotton, wool, silk, linen, nylon, polyethylene glycol terephthalate (e.g., Dacron), regenerated cellulose rayons, cellulose acetate, casein, vinyl resin fibers, such as copolymers of vinyl chloride and vinyl acetate or acrylonitrile, and especially polymers containing from 75 to 95% by weight of acrylonitrile such as Orlon and Acrilan. The proportion of fibers, filaments, or yarns formed of the aminolyzable addition polymer, cross-linked polymer, or aminolyzed polymer, in the fabrics may vary widely from 1 to 100%. For some purposes, a proportion of 1 to 10% may be entirely adequate such as in modifying the dyeability or the resistance to static electricity. In other fabrics, proportions of over 10%, such as from 15 to 50% may be desired; whereas for the preparation of industrial fabrics intended for ion-exchange purposes, the proportion is preferably over 50%, such as from 80 to 100%.

Among the fabrics contemplated by the present invention are those in which there may be a reinforcing element to improve the strength of the fabric in various ways. This reinforcing element may be, for example, a glass yarn woven at intervals through a woven fabric comprising the yarns formed of fibers of the present invention arranged in alternate relationship with the glass-fiber or -filament yarns. Pile and other tufted fabrics are also contemplated which may be formed entirely or partly of the special aminolyzable, aminolyzed, or cross-linked fibers. For example, the fabric may be formed of a base or backing fabric, especially a woven fabric, made of reinforcing yarns such as of glass filament yarns, and a pile, or some or all of the tufted portion of the fabric, formed of the special fibers or filaments of the present invention.

The fabric may comprise potentially adhesive fibers adapted to bond fibers in the fabric together as a result of being rendered tacky by application of heat or solvents or both. The vinyl resin fibers such as copolymers of vinyl chloride and vinyl acetate are representative of this type of element.

An essential feature of the fabrics of the present invention is that they comprise at least 1% of fibers or filaments formed of the special cross-linked addition polymers.

The fibers of the present invention may be obtained by forming fibers of a polymer of 50 to 100 mole percent of at least one monomer selected from the group consisting of methyl acrylate, ethyl acrylate, acrylamide, methacrylamide, N-alkyl-substituted acrylamide, and acrylonitrile. These polymers are hydrolyzable and aminolyzable and at some time before, during, or after conversion into a fabric, they are aminolyzed by reaction with certain diamines as described hereinafter.

Alternatively, the fibers may be formed by the spinning of polymers containing tertiary amine groups. Examples include linear copolymers of 1 to 99% by weight of dimethylaminoethyl methacrylate or acrylate, or of N-dimethylaminoethyl acrylamide or methacrylamide with other copolymerizable monoethylenically unsaturated monomers. Other comonomers that may be used include aminoalkyl acrylates, methacrylates, or itaconates, e.g., β -aminoethyl acrylate, methacrylate, or itaconate diester, 5-aminopentyl methacrylate or itaconate diester, β -morpholinoethyl acrylate, methacrylate, or itaconate diester, 3-aminopropyl acrylate, methacrylate, or itaconate diester,

2-amino-2-methylpropyl acrylate, methacrylate or itaconate diester, β -N-methylaminoethyl acrylate, methacrylate, or itaconate diester, β -N,N-dimethylaminoethyl acrylate, methacrylate, or itaconate diester; N-aminoalkyl acrylamides, methacrylamides, or itaconamides, e.g., N- β -amino-ethyl acrylamide or methacrylamide, N-5-aminopentyl acrylamide or methacrylamide, N,N-di- β -aminoethyl acrylamide or methacrylamide, N,N-di- β -methylaminoethyl acrylamide or methacrylamide, N,N-di- β -dimethylaminoethyl acrylamide or methacrylamide, N- β -diethylaminoethyl acrylamide or methacrylamide, vinyloxyalkylamines, e.g., β -vinylxyethylamine, dimethyl-(β -vinylxyethyl)-amine, vinylthiolalkylamines, such as dimethyl-(β -vinylthioethyl)-amine; quaternary ammonium compounds obtained by the alkylation of any of the amines so far mentioned by alkylating agents (which is herein intended to include aralkylating agents and substituted aralkylating agents), such as methyl chloride, ethyl chloride, benzyl chloride, allyl chloride, substituted allyl chloride, e.g., dodecylallyl chloride, dodecenyl chlorides, alkylbenzyl chlorides, e.g., octylbenzyl chlorides (from diisobutylene), any chloromethylated aromatic-like compound, e.g., chlorobenzyl chloride, chloromethylated thiophene, chloromethylated furane, chloromethylated naphthalene, or corresponding bromides or iodides, e.g., phenoxyethyl bromide, methyl iodide; dimethyl sulfate, dimethyl sulfite, dimethyl phosphite, ethylene oxide, propylene oxide, styrene oxide, and butylene oxide. For example, a mixture of 17.9 grams (0.109 mole) of monomeric dimethylaminopropylacrylamide, 13.8 grams (0.109 mole) of benzyl chloride, 74 grams of absolute ethanol (30% solids) and di- β -naphthol was heated to reflux for two hours. The product was isolated by concentration in vacuo. Any of the quaternary ammonium monomeric compounds disclosed in copending United States applications Serial No. 441,643, filed July 6, 1954, now Patent 2,980,657; Serial No. 461,285, filed October 8, 1954, now Patent 2,980,634; Serial No. 495,784, filed March 21, 1955 now patent 3,008,851; and in the United States Patents 2,810,713 and 2,840,546, all in the hands of a common assignee may be used. Examples of these quaternary compounds include (β -methacryloxyethyl)trimethylammonium hydroxide, chloride, methosulfate, bromide, and so on, the dodecenyl chloride quaternary of 1-(β -dimethylaminoethyl)-3-vinyl-imidazolidinone-2 and the benzyl chloride quaternary of 1-(β -dioctadecylaminoethyl)-3-vinyl-imidazolidinone-2, (β -acryloxyethyl)trimethylammonium chloride, hydroxide, and so on, (β -methacrylamidoethyl)triethylammonium chloride, hydroxide, and so on, (β -vinylxyethyl)trimethylammonium chloride, hydroxide, and so on.

The copolymers that are formed into fibers may contain, besides the aminolyzable units and/or the amine-containing units, additional inactive units, that is units which are unaffected by the polyfunctional cross-linking agent or by the aminolyzing agent, or by both. Such additional comonomer units may be termed inactive units. Examples of such units include vinyl chloride, vinyl esters of organic acids, such as acetic, butyric, propionic, lauric, and so on acids, ethylene isobutylene, styrene, vinyltoluene, methacrylonitrile, vinylidene chloride, vinyl ethers, such as methyl vinyl ether and so on.

In accordance with a preferred embodiment of the present invention, fibers or continuous filaments are formed of the aminolyzable polymers just described. These fibers are preferably oriented by stretching, such as from about 50% to several thousand percent of their original length, in order to improve their tensile strengths. If the fibers do not have the desired amount of amine groups needed later for cross-linking, dye-modification, resistance to static electricity, or the like, such groups should be introduced by aminolysis before stretching. After stretching, the fibers which now contain amine groups are treated to effect cross-linking by reaction with

a polyfunctional alkylating reactant, such as an organic dichloride. The cross-linking stabilizes the oriented structure so that it resists shrinkage at elevated temperatures. Depending on the conditions of the cross-linking reaction, it may or may not be necessary to hold the fibers, filaments, or yarns being subjected to the reaction in such a manner as to prevent shrinkage during the treatment.

After the fibers are cross-linked, they can be further reacted, if desired, to introduce an additional proportion of ion exchange groups, either of cationic carboxyl groups or of anionic amine or quaternary ammonium groups, such as by hydrolysis or aminolysis of the acrylic acid ester, amide, or nitrile units of the cross-linked polymer. This reaction can be effected on the fibers or filaments before or after they are made into fabrics, such as yarns, woven or knitted fabrics, "non-woven" web fabrics, or other types of fabrics as described above, but is preferably performed, if needed, exclusively on the fibers or filaments before stretching.

Thus, in accordance with the invention, there is first obtained or produced a linear addition polymer as defined above containing amine groups or quaternary ammonium groups or containing units of methyl or ethyl acrylate, an acrylamide, or acrylonitrile, which may be called precursory units and are adapted to be converted by subsequent treatment into ion-exchange groups including carboxyl groups, amine groups, and quaternary ammonium groups. It is characteristic of the fabrics of the present invention that they comprise fibers formed of cross-linked polymers which contain at least one-half mole percent of units containing groups selected from the group consisting of carboxyl, amine, and quaternary ammonium groups, preferably at least 7 mole percent thereof, and may contain up to about 99 mole percent of units containing such groups, there being from one-half to 30 mole percent of cross-linked units.

The polymers of these various units may be produced by bulk, solution, emulsion or suspension procedures. In the copolymerization the usual initiators or catalysts may be used, of which the following are typical: α,α' -bis-azoisobutyronitrile, dimethyl azobisisobutyrate, 2,2'-azobis-2,4-dimethylvaleronitrile, benzoyl peroxide, acetyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, di-tert-butyl peroxide, tert-butyl perbenzoate, stearoyl peroxide, cumene hydroperoxide, and "per-salts" such as ammonium persulfate and ammonium perborate. The catalysts are used in amounts from 0.2% to 5%, and preferably from 0.5% to 2%, based on the weight of the polymerizable compound or compounds.

The polymerization may be effected at temperatures from about room temperature up to about 100° C. for periods of time ranging from a few minutes to several hours. In producing aqueous emulsion copolymer dispersions, any of the initiators above may be used, but it is generally preferable to use ammonium, sodium, or potassium persulfate in conjunction with a reducing agent, such as a sulfite, bisulfite, metabisulfite or hydrosulfite of an alkali metal, to provide a redox system. The addition of a few parts per million of a polyvalent metal, such as iron, may also be used in the emulsion polymerization procedure. The monomer or mixture of monomers may be added gradually or in successive increments at spaced intervals through the polymerization or the entire monomer or monomer mixture may be polymerized as a single batch, regardless of which polymerizing system or technique is employed.

As emulsifiers when emulsion polymerization is employed, there may be used any of the conventional anionic, cationic, or non-ionic emulsifiers, such as fatty acid soaps, including sodium oleate, sodium laurate, sodium stearate and so on, also sodium dodecylsulfate or sulfonate, sodium pentadecylbenzenesulfonate, sodium octylphenoxyethoxyethylsulfonate, octylphenoxypolyethoxyethanol, tetradecylthiopolyethoxyethanol, ethylene oxide condensates of tall oil and other long-chained fatty acids, lauryl-

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dimethylbenzylammonium chloride, dodecylbenzyltrimethylammonium chloride, or any of the many wetting agents and emulsifiers which are generally advocated for forming aqueous emulsions. Some emulsifiers are better for handling a given monomer or a mixture of monomers than others.

The product obtained by bulk polymerization may be directly used in a melt-spinning or the polymeric product thereby obtained may be dissolved in a suitable solvent, such as water if the polymer is soluble therein or an organic solvent in which it is soluble, and the dissolved polymer may be spun either by a wet or a dry system, using as coagulants in the wet-spinning, organic liquids which are not solvents for the polymer but are solvents for the water when aqueous solutions are spun and either aqueous media or organic solvents in which the polymer is insoluble but in which the solvent of the spinning solution is soluble when solutions in organic solvents are spun or extruded through slot orifices to produce films. The product obtained by solution polymerization may be directly wet- or dry-spun or the polymer thereof may be precipitated or in some other manner coagulated and dissolved in another solvent to prepare a spinning solution. The precipitated or coagulated polymer may also be spun by melt-spinning if desired. Similarly, the product obtained by suspension polymerization may be recovered and used in melt-spinning or dissolved in a suitable solvent and either wet- or dry-spun. The aqueous dispersions obtained by emulsion polymerization may be directly spun either by a wet- or a dry-spinning system or the polymer therein may be coagulated and then spun by a melt-spinning operation or by a wet- or dry-spinning operation.

The spinning of the polymer mass, either as a molten polymer or as a solution or dispersion thereof, is then carried out, as more particularly described hereinafter, to form films, filaments, fibers or pellicles or the like; and after the formation of such structures, treatment is carried out to effect the cross-linking of the polymer. If stretching is employed, substantially all of the cross-linking should be effected after the stretching.

The precursory units of the polymer are all hydrolyzable to produce carboxyl units having cation-exchange capacities. They also serve as precursors for the introduction of anion-exchange groups, such as amine groups and quaternary ammonium groups. Thus, aminolysis of these methyl or ethyl acrylate, acrylonitrile, and/or any acrylamide units may be effected with polyamines, and especially diamines having a tertiary nitrogen atom and another which is either primary or secondary, such as dimethylaminoethylamine or any of those mentioned in column 3, lines 17 to 33, of copending application Serial No. 441,643, filed July 6, 1954, now Patent 2,980,657, which latter list is incorporated herein by reference. Especially advantageous polyamines for this purpose are those disclosed in the passage from line 43 of column 2 to line 75 of column 3 in Melamed U.S. Patent 2,845,408, which group of polyamines is incorporated herein by reference. One preferred example of this type of amine is β -(N-t-butylamino)ethylamine and the characteristic that makes these polyamines outstanding is the stability of the aminolyzed polymer products obtained in spite of the presence of one or more hydrogen atoms on each terminal nitrogen of the amine groups in the aminolyzed polymer. This stability is apparently the result of the presence of the tertiary carbon atom attached directly to the nitrogen atom. The amine-containing units may then, if desired, be converted to quaternary ammonium-containing units by alkylation by means of any of the alkylating agents mentioned hereinabove. The aminolysis and quaternization may be effected in the same way as in Serial No. 441,643, now Patent 2,980,657, or in United States Patent 2,845,408, above, and the disclosure therein of amines used alkylating agents used, and the

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procedures and conditions for aminolysis and quaternization are incorporated herein by reference.

Cross-linking may be effected by quaternization by means of poly-halides and especially di-halides, alkylene dihalides having 1 to 10 carbon atoms, such as methylene dichloride or dibromide, ethylene dichloride, dibromide, or diiodide, hexamethylene dichloride and the like, and aralkylene di-halides having 8 to 10 carbon atoms, such as o-, m-, or p-xylylene dichloride, dibromide, or diiodide. The fibers or filaments may be formed of homopolymers of monomeric amines, such as of diethylaminoethyl methacrylate whose units have anion-exchange characteristics and are cross-linkable by the di-halides just mentioned.

The general procedure for spinning is as follows:

The polymers may be formed into fibers or filaments by extrusion, either of a melt of the polymer, a solution thereof in water, if soluble therein, or in an organic solvent or an aqueous dispersion of the copolymer if it is water-insoluble, through an extrusion device containing one or more orifices into a suitable coagulating medium which may be a cooling fluid, gaseous or liquid, in the case of melt-spinning; a heated atmosphere in the case of the dry-spinning of a solution or aqueous dispersion; or a coagulating liquid in the case of wet-spinning a solution or aqueous dispersion. Fibrous structures may also be formed by a spraying technique and so-called "cocoon" protective coverings may also be formed by spraying.

In the melt-spinning of the polymers, provision is made for bringing the polymer mass, which may preferably be in granular or pulverized form, into molten condition in proximity to the spinneret or other extrusion device. This is generally accomplished by providing a suitably heated chamber in proximity to the spinneret or other extrusion device and super-imposing upon the molten mass suitable pressure for forcing the mass through the orifice or orifices of the device. A cooled atmosphere of carbon dioxide, nitrogen, helium, or the like may be maintained within the space into which the molten polymer stream or streams is or are extruded. The temperature of the atmosphere may be from -50° to about 20° C.

Dry- and wet-spinning procedures may be employed with solutions of the polymers in water, if soluble therein, or in organic solvents, such as acetone, dioxane, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide, acetonitrile, nitromethane, nitroethane, and so on. The concentration of the copolymer in such solutions may be from about 15% to 25%. Similarly, aqueous dispersions of the copolymers made by emulsion copolymerization in aqueous media may be formed into fibers, films and the like by either dry- or wet-spinning. The concentration of the copolymer in the aqueous dispersions may be from 20 to 70% in wet-spinning or from about 40 to 70% in dry-spinning. Preferably, a concentration of 30 to 50% is used in wet-spinning and about 50 to 55% in dry-spinning. In the dry-spinning of solutions or dispersions of the polymers, the stream or streams of the solution or dispersion issuing from the orifice or orifices of the extrusion device are generally subjected to a heated atmosphere immediately after issuance and for a considerable distance as they travel away from the extrusion device. This is generally effected in a chamber referred to as a spinning cell in which the heated atmosphere is introduced, either near the extrusion device when concurrent flow is desired or at the discharge end of the device when countercurrent flow is desired. The heated atmosphere may have a temperature within the cell ranging from about 30° C. up to 300° C. Generally, if the spinning solution used is made with a volatile organic solvent, the temperature may be in the lower portion of this range, such as from about 30° to 90° C., whereas when an aqueous solution or aqueous dispersion is being spun, higher temperatures are generally employed in the cell. Specifically, when spinning an aqueous dispersion of an emulsion copoly-

mer, temperatures of 180° to 400° C. may be employed. In any event, if the filmy structure is formed of a polymer in which the cross-linkable units are self-cross-linking on heating, and it is desired to stretch the structure, excessive temperature or prolonged exposure thereto should be avoided to minimize cross-linking at this stage.

Generally, the formed structures are completely coalesced by the time they leave the spinning cell. However, in the event that the duration and intensity of heat treatment in the spinning cell is inadequate to completely coalesce the polymer particles within the formed structure when an aqueous copolymer dispersion is spun, an additional heating stage may be provided to complete the coalescence. This heating is performed at a temperature sufficiently high to carry the temperature of the shaped structure above the T_1 value (apparent second order transition temperature) of the copolymer and preferably at least about 30° above the T_1 value thereof.

The apparent second order transition temperature, here symbolized as T_1 , is defined as that temperature at which the first derivative of thermodynamic variables, such as coefficient of expansion or heat capacity, undergoes a sudden change. The transition temperature is observed as an inflection temperature which is conveniently found by plotting the log of the modulus of rigidity against temperature. A suitable method for determining such modulus and transition temperature is described by Williamson in British Plastics, 23, pages 87-90. The T_1 values here used are generally those temperatures at which the modulus is 300 kg./cm.². The T_1 values referred to are for polymers as such in a dry state unless otherwise designated.

The products, after leaving the spinning cell (whether dry-spinning, wet-spinning, or melt-spinning is used), may then be stretched to any extent desired, such as from about 5% to over 1000% of the length they have before stretching. Preferably, at least 50% stretch is performed on the fiber.

In the wet-spinning of either solutions or aqueous dispersions of the copolymers, the liquid coagulating bath may be aqueous baths containing electrolytes, such as acids, alkalis, or salts. Generally, the electrolyte content should be from 5% to 50% and the temperature of the bath from about 20° to 105° C., preferably 30° to 45° C. However, when acid baths are used, much lower concentrations even as low as about ½ percent are effective to lower the pH to a value of 6 or less. Mixtures of the above electrolytes may be employed, such as an acid bath containing salts or an alkaline bath containing salts. Acid baths may be composed of aqueous solutions containing from ½ to 98% of an acid such as sulfuric acid or other inorganic acids such as hydrochloric, phosphoric, boric, or sulfamic, or of organic acids such as oxalic, formic, acetic, citric, lactic, or an alkanesulfonic acid or arylsulfonic acid, such as ethanesulfonic or toluenesulfonic acids. The bath may have a pH value from about 1 to 6 and preferably between 1½ and 4. The bath may contain, besides the acid, buffering salts such as sodium dihydrogen phosphate. The acid baths may also contain small amounts of polyvalent metal salts, such as sulfates, chlorides, or the like, of iron (either ferrous or ferric), aluminum, zirconium, tin, cobalt, nickel, and zinc.

Alkaline baths may also be used as the coagulating baths for wet-spinning operations. The pH may be from 8 to 13 and is preferably at least 12 when aqueous dispersions of emulsion copolymers are used. To make up the alkaline baths, there may be used any water-soluble electrolytes or mixtures thereof, such as sodium chloride, lithium chloride, potassium chloride, sodium carbonate, sodium sulfate, sodium acetate, potassium sulfate, sodium or potassium formate, or sodium phosphates of various types including complex phosphates, alkalis, such as sodium or potassium hydroxide, or mixtures of such electrolytes may be used. Alkalinity may also be

supplied by a quaternary ammonium hydroxide such as trimethylbenzylammonium hydroxide, hydroxyethyltrimethylammonium hydroxide, or dimethyldibenzylammonium hydroxide. Organic materials such as glucose and urea may also be present in the bath.

Acidic, neutral or alkaline baths containing, as the major component of the solute, salts such as neutral, acidic or basic salts may be employed. For example, a coagulating bath may be composed of aqueous solutions of sodium sulfate, sodium chloride, ammonium chloride, sodium carbonate, sodium bisulfite, sodium acetate, borax, aluminum chloride, and so on.

Wet-spinning may also be performed by extrusion of the solution or dispersion of the polymer into organic liquids which are non-solvents for the polymer but are solvents for the water or organic liquid used for dissolving the polymer to make the spinning solution.

The immersion of the filaments or films in the coagulating bath may vary from a fraction of an inch, such as from ¼ to ½ inch to several feet, such as three to four feet or more. In wet-spinning, the filaments, after removal from the coagulating bath, may be treated with a neutralizing agent, such as an aqueous acid solution when an alkaline coagulating bath is used. Whether or not neutralization is first effected, rinsing may be effected such as with water or even with organic liquids, but preferably with water.

The spinneret or like extrusion device may be fed with the dispersion from a suitable feed- or supply-tank by a constant pressure or constant displacement method. This may be accomplished by the use of an oil ram operated either pneumatically, hydraulically, or mechanically. Where no harm is done when the dispersion is subjected directly to air pressure or to the pressure of a suitable gas, compressed air or gas may be introduced into the tank directly over the dispersion under the control of a suitable pressure regulating system in conventional manner. When the dispersions have satisfactory stability against mechanical shear, they may be fed to the spinnerets by suitable pumps and especially the conventional gear pumps which may be provided with the conventional by-pass for controlling the pressure.

The size of the orifices of the spinneret may be from about 0.5 to 10 mils or more up to 20 mils in diameter. For fine filaments, the usual size of orifices, namely 2.5 to 4 mils in diameter, may be used; whereas for larger filaments, orifices having diameters of 5 to 9 mils may be used. Orifices of even larger size may be used to produce monofilaments, and, besides having a round cross-section, they may be of various cross-sections such as oval, elliptical, or of a rectangular slit or slot-like shape to produce ribbons or films of various widths.

The films or filaments may be withdrawn from the extrusion device at the same speed as the linear speed of extrusion or at a speed which is considerably higher or considerably less than the speed of extrusion. For example, the withdrawal speed may be used which is as low as 20% of the linear speed of extrusion or a speed of twice to three times the linear speed of extrusion. The speed of withdrawal may vary from one meter to 100 meters per minute or higher. When a film is produced, it may be wound on a mandrel after completion of the cross-linking operation and preferably after the cross-linked film has been dried. When filaments are produced, they may be collected by winding on a bobbin or on a centrifugal bucket or pot, the latter having the advantage of imparting a small amount of twist, such as from 1½ to 2½ turns per inch to the filament bundle or yarn when a multi-holed spinneret is used. Collection is preferably made after completion of the cross-linking and drying operations.

During the stretching of the filaments or films, they may be heated to temperatures of 70° to 300° C. by passage through a heated atmosphere or over a smooth heated plate such as of metal. The extent of stretch

may be controlled such as by arranging the heated atmosphere or plate, through or over which the filaments or films pass, between a pair of wheels or godets which have the desired difference in speed so that the linear velocity of the filaments about the periphery of the second godet is a pre-determined greater value from 50 to 1000% or more greater than the peripheral velocity of the first godet.

When an aqueous copolymer dispersion is spun, a fusion-aid may be employed. These materials may be introduced into the aqueous polymer dispersion either before emulsion polymerization of the monomers or after such polymerization. Compounds effective for this purpose have solubility in the polymer and have a favorable distribution coefficient in a polymer-water system. A copolymer of 70 parts of acrylonitrile, 5 parts of a cross-linking comonomer, and 25 parts of 3,3,5-trimethylcyclohexyl acrylate may be used with adiponitrile, α -methylsuccinonitrile, and nitromethane.

Also effective as fusion-aids for polymers formed in major proportion from acrylonitrile or methacrylonitrile are phenylacetonitrile, butyronitrile, hexanenitrile, α -methylsuccinonitrile, acrylonitrile, or methacrylonitrile monomers, endomethylenetetrahydrobenzonitrile, succinonitrile, benzonitrile, isobutyronitrile, and furonitrile.

Toluene, xylene, chlorinated hydrocarbons, such as chloroform and ethylene dichloride, ethyl acetate and butyl acetate are useful fusion-aids for copolymers of 80% methyl methacrylate and 20% of ethyl acrylate. From 1 to 40% by weight of a fusion-aid based on the weight of the copolymer may be used, 10 to 20% being preferably used.

When the fibers or films have been stretched longitudinally, the polymer molecules are at least partially oriented along the fiber axis or lengthwise of the film and the extent of orientation depends on the degree of stretch. Heating such fibers or films very quickly causes shrinkage or retraction and loss of a great deal or all of the orientation at relatively low temperatures. By subjecting the stretched fibers or films to the cross-linking procedure of the present invention, the temperature at which substantial shrinkage of the fiber or film occurs is elevated substantially and the extent of shrinkage at a given elevated temperature, such as at 200° C. for example, is greatly reduced.

As stated previously, the cross-linking operation may be effected at any stage of the fiber- or filament-forming process. For example, it may be performed upon the freshly-formed fibers directly after they are removed from the spinneret in a melt-spinning operation. However, it is generally preferable, in order to provide structural products having increased strengths, to stretch the products before effecting the cross-linking thereof. Of course, if in the particular products desired, there is no need for orientation or stretching to impart greater strength to the products, whether fibers or films, the cross-linking may be effected soon after the coalescence of the polymer into the fibrous or pellicular form has been completed. However, when aqueous copolymer dispersions are spun either by a wet-spinning or dry-spinning operation and a so-called "fuse-drying" step is employed to effect complete coalescence of the particles into a continuous mass, it is generally desirable and, in most cases, essential that the fuse-drying, which is effected at relatively high temperatures of at least 30° C. above the T_i value of the copolymer (such as from 60° C. to 400° C.), be effected before the cross-linking is effected.

The filaments, fibers, films or threads, cords and fabrics formed thereof may be subjected to other customary finishing processes, such as crimping, curling, twisting, sizing, softening, or lubricating to facilitate weaving, knitting and other textile operations.

The filaments, threads or yarns produced by the above described procedural steps are useful in the preparation

of various types of fabrics. They are useful in fabrics where controlled shrinkage is desired as in filter cloths.

Uncross-linked fibers or filaments of the present invention, and especially those formed from copolymers containing one-half to 30 mole percent of cross-linkable units, whether stretched or unstretched, may be converted into fabricated structures before the cross-linking is effected by alkylation of the polymer, and then at some stage during or after the fabrication, the cross-linking may be performed upon the fabric. It is preferred, however, to have the fibers or filaments in cross-linked condition before fabrication.

Fabricating procedures that may be employed include the formation of yarns by twisting together of continuous filaments or by the drafting and twisting of staple fibers formed of the polymers. Also included are plied yarns or cords obtained by doubling two or more of the twisted yarns obtained either from continuous filaments or staple fibers. Besides the yarns and cords, textile fabrics may be formed therefrom by weaving, braiding, or knitting of the yarns. Non-woven fabrics are contemplated in which the fibers formed of the cross-linked polymers containing ion-exchange groups are distributed haphazardly to form a felt-like or paper-like structure either of low density or of compact structure. For example, such non-woven fabrics may be produced by carding the polymer fibers with or without additional fibers of textile type or paper-making length, such as of woodpulp, cotton, silk, rayon, wool, linen, nylon, polyethylene terephthalate and so on, and subsequently rendering some of the fibers in the products adhesive by heating. The fibers formed of polymers containing the ion-exchange groups may be relied on for adhesion, in which event the heating thereof in the fabricated structure, mat, woven or knitted textile or the like to tacky condition may be followed by treatment with a cross-linking agent and heating to effect cross-linking and thereby impart reduced swelling, shrinkage, and obtain insolubilization and stabilization of the adhered fibers in the structure.

As pointed out hereinabove, the fabrics of the present invention are quite advantageous and have a wide variety of uses. In textile products, the presence in the fibers of polymers containing 0.5 to 10 mole percent of units containing ion-exchange groups imparts advantageous moisture regain properties and reduces the tendency to develop static charges on rubbing. The latter property is extremely important in many fabrics including automobile seat covers. Fabrics comprising fibers having from about 10 to about 99 mole percent of units containing ion-exchange groups are advantageous in numerous other uses. For industrial ion-exchange uses, the fibers in the fabrics should preferably be made from polymers containing at least 25 mole percent of ion-exchange groups. They are useful as wash cloths (for both face- and dish-washing purposes) in which utility they remove ions from the water that is employed. They may, of course, be readily regenerated by soaking in an alkaline medium. The pile and tufted fabrics are particularly useful when they contain ion-exchange groups in the larger range specified for use as ion-exchange media. The pile or height of tuft in such fabrics may vary extensively. Generally, a thickness of 0.05 to 1 inch or more is quite advantageous. Of the fabrics formed of fibers containing polymers having amine groups (by which term quaternary ammonium groups are not included) those containing tertiary amine groups or amine groups having a tertiary carbon atom directly attached to the nitrogen atom are preferred for industrial ion-exchange or ion-absorption usage because of their greater stability. Thus, they can be used for treatment of solutions containing sugars or other aldehydes; whereas ordinary primary and secondary amine groups are generally less suitable for these purposes because of their greater reactivity toward aldehydes.

The fibrous products of the present invention are ion-exchanging resins in a special form adapting them to be

applied in a wide variety of ways for the general purposes which are served by such resins including anion-exchange activity, catalytic activity, and other chemical functions including oxidative activity. They may be modified to enhance any of the particular activities. For example, any of the anion-exchange resin products of the present invention may be treated with an anionic ceric salt, such as an anionic ceric sulfate or nitrate complex in the manner disclosed in a copending application Serial No. 537,558, filed September 29, 1955, now Patent 2,906,714 (in the hands of a common assignee) to provide oxidative resins having a wide variety of uses where a solid oxidizing agent may be desirable. Thus, such oxidative resins in fiber form may be incorporated in filters used in tobacco products, such as cigars, cigarettes, or in smoker's pipes to oxidize and/or absorb organic and inorganic components of the smoke drum through the filter by the smoker. Fine fibers are preferred to provide the maximum surface for carrying the ceric salt. The preparation of these oxidative resins from the anion-exchange resins in film or fiber form is effected in the same ways as those used in United States application Serial No. 537,558, filed September 29, 1955, for converting particulate anion-exchange resins into the oxidative ceric salt complex modification and the disclosure of said application is incorporated herein by reference.

In the examples, parts and percentages are by weight unless otherwise indicated:

Example 1

(a) To 200 parts of distilled water at room temperature is added 6 parts of an aqueous solution containing 2% of ferrous sulfate heptahydrate and 4% of the sodium salt of ethylene-diaminotetraacetic acid adjusted to pH 4 with 0.5 N sulfuric acid solution. Then 3 parts of sodium laurate is added followed by 0.6 part of sodium formaldehyde sulfoxylate·2H₂O. The pH of the solution is adjusted to 10.5 with 0.5 N NaOH. A mixture of 60 parts of acrylonitrile, 40 parts of methyl acrylate, and 10 parts of adiponitrile is added with stirring, and the air above the resulting emulsion is replaced by nitrogen. To the emulsifier is now added 0.15 part of phenylcyclohexane hydroperoxide as a 10% solution in toluene. After a short induction period, polymerization starts as evidenced by a sharp temperature rise. The temperature is now controlled by cooling to remain in the range 35° to 40° C. Over 85% conversion to a dispersion of fine particle size (less than 0.1 micron in diameter) is achieved in about one-half hour after addition of the phenylcyclohexane hydroperoxide. The polymer contained in this dispersion has a T₁ of about 85° C. to 95° C.

(b) The dispersion is concentrated to 55% polymer solids by evaporation at about 100 mm. Hg absolute pressure. The concentrated dispersion is forced at a rate of 7.0 meters per minute through a spinneret having 5 holes which are 0.0025 inch in diameter downward into a vertical tower through which nitrogen at 220° C. is passed. The filaments are collected at a rate of about 70 meters per minute, and subjected to a temperature of 260° C. for a few seconds in order to assure complete fusion of the particles. The yarn is then treated with a solution comprising 50 parts of dimethylaminopropylamine and 50 parts of dodecane at 142° C. for one hour. The yarn is then stretched about 200% at about 120° C. and treated with 20% p-xylylenedichloride in toluene at 50° C. at constant length and cured at 150° C. at constant length for 30 minutes. The yarn is then soaked in a mixture of 60 milliliters of N/20 NaOH and 60 milliliters of ethanol per gram of yarn for about two days at 60° C. The resulting yarn has a cation-exchange capacity of about 2.5 milliequivalents per gram.

(c) The yarn of part (b) is fabricated into a woven fabric which serves as a filter fabric.

(d) The woven fabric of part (c) is fashioned into wash cloths. In the wash water for washing dishes, the face, hands, or other parts of the human body, the cloths soften the water, reduce the consumption of soap, and improve the washing efficiency generally.

Example 2

(a) A dispersion of a copolymer of 50 parts of acrylonitrile and 50 parts of methyl acrylate is prepared by a procedure similar to that described in Example 1 (a). The dispersion, at about 35% polymer solids, is spun into 4% hydrochloric acid at 75° C. using a 40-hole platinum alloy spinneret with a hole diameter of 0.0025 inch. The rate of draw from the spinneret is 9 meters per minute and the length of immersion is 4 inches. The yarn is washed in water at 60° C. and then in 0.5% borax at 60° C. and dried in contact with a roll coated with polytetrafluoroethylene at 240° C. The yarn is then treated with a solution comprising 40 parts of dimethylaminopropylamine and 60 parts of dodecane at 140° C. for 1½ hours. It is then stretched about 300% while being heated to 110° C. and allowed to cool in the stretched condition. The stretched yarn is treated with 10% p-xylylene dichloride in toluene at 50° C. at constant length for one hour and cured at 150° C. at constant length for 40 minutes. The resulting yarn has an anion-exchange capacity of about 2.2 milliequivalents per gram.

(b) The yarn is then fabricated into a knitted fabric and the resulting fabric is converted into an endless belt which serves as an ion-exchange medium in a continuous system in which the belt is driven by rollers alternating through one liquid containing ions to be exchanged or removed, and through another constituting a regenerating bath, of dilute alkali, guide rollers in the containers for the liquids directing the fabric belt there-through.

Example 3

(a) The procedure of Example 2 (a) and (b) is repeated except that the stretched yarn is treated with a solution of 10% p-xylylene dichloride and 20% benzyl chloride in toluene instead of the 10% p-xylylene dichloride solution in toluene.

(b) The product of part (a) is treated with 5% sulfuric acid to convert it to the sulfate.

(c) The resinous fibers are supported in a glass tube and through the bed or column of fibers there is slowly passed an aqueous solution containing 26.4 grams of the ceric salt, tetrasulfato-ceric acid of the composition Ce(HSO₄)₄, and 50 ml. of 96% sulfuric acid per liter of solution. The fibers are rinsed with deionized water, dried, and formed into a cylindrical filter wad for insertion into the end of a cigarette.

(d) A plurality of treated yarns obtained in part (a) hereof are assembled into a large-denier tow and cut into staple fiber of 1-inch length. The fiber is opened and carded. Four carded webs are superposed with the machine direction of alternate layers alternating with that of the others. Fibers in the non-woven fabric thus obtained are bonded by a binder formed of a polymer of ethyl acrylate introduced by impregnation with a 40% emulsion-polymerized ethyl acrylate and then drying the impregnated fabric at 140° F. to bind fibers therein.

In the specification and claims, the expression "fabric" is intended to embrace yarns and other fiber or filament assemblages as well as woven, knitted, "non-woven," and other types of fabrics containing interlocked fibers or yarns.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims. This application is a continuation-in-part of our copending ap-

lication Serial No. 587,925, filed May 29, 1956, now U.S. Patent 2,933,460.

We claim:

1. As an article of manufacture, a fabric comprising interlocked fibers formed of a cross-linked product of a linear addition polymer containing one-half to about 100 mole percent of polymerized units having tertiary amine groups, the linear polymer molecules having from one-half to 30 mole percent of such tertiary amine groups alkylated while the linear polymer molecules are in fiber form, by a polyhalide alkylating agent having 1 to 10 carbon atoms in which the halide is selected from the group consisting of chloride, bromide, and iodide, in the cross-linked product whereby the latter is resistant to shrinkage.

2. An article as defined in claim 1 in which the fibers are deposited in haphazard array.

3. As an article of manufacture, a fabric comprising interlocked yarns comprising fibers formed of a cross-linked product of a linear addition polymer containing one-half to about 100 mole percent of polymerized units having tertiary amine groups, the linear polymer molecules having from one-half to 30 mole percent of such tertiary amine groups alkylated while the linear polymer molecules are in fiber form, by a polyhalide alkylating agent having 1 to 10 carbon atoms in which the halide is selected from the group consisting of chloride, bromide, and iodide, in the cross-linked product whereby the latter is resistant to shrinkage.

4. An article as defined in claim 3 in which the fabric is a woven fabric.

5. As an article of manufacture, a pile fabric comprising in at least the pile thereof, fibers formed of a cross-linked product of a linear addition polymer containing one-half to about 100 mole percent of polymerized units having tertiary amine groups, the linear polymer molecules having from one-half to 30 mole percent of such tertiary amine groups alkylated while the linear polymer molecules are in fiber form, by a polyhalide alkylating agent having 1 to 10 carbon atoms in which the halide is selected from the group consisting of chloride, bromide, and iodide, in the cross-linked product whereby the latter is resistant to shrinkage.

6. As an article of manufacture, a textile fabric comprising a plurality of fibers having at least one small

dimension of the order of one-tenth to twenty mils comprising a cross-linked product of a linear addition copolymer of monoethylenically unsaturated copolymerizable molecules comprising one-half to about 99 mole percent of units containing ion-exchange groups selected from the group consisting of carboxyl, amine, amine salt, quaternary ammonium groups, and mixtures thereof, from one-half to 30 mole percent of the units in the linear polymer molecules being connected by alkylation of tertiary amine groups therein while the linear polymer molecules are in fiber form, by a polyhalide having 1 to 10 carbon atoms in which the halide is selected from the group consisting of chloride, bromide, and iodide, to form cross-linkages comprising quaternary ammonium groups, said fibers having an ion-exchange capacity of at least 2 milliequivalents per gram.

7. A fiber as defined in claim 6 in which the alkylating agent is p-xylylene dichloride.

8. As an article of manufacture, a textile fabric comprising a cross-linked product of a linear addition copolymer of (A) at least one member selected from the group consisting of methyl acrylate, ethyl acrylate, an acrylamide, and acrylonitrile, and (B) at least one member selected from the group consisting of acrylic acid and N-di(C₁-C₄)-alkylamino(C₂-C₄)alkyl-acrylamide, from one-half to 30 mole percent of amino-containing units in the linear polymer molecules being formed into cross-linkages by alkylation while the linear polymer molecules are in fiber form, with a dihalide having 1 to 10 carbon atoms in which the halide is selected from the group consisting of chloride, bromide, and iodide.

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