United States Patent Office 3,079,280 Patented Feb. 26, 1963

3,079,280

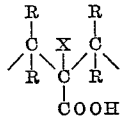
TREATMENT OF FIBROUS TEXTILE MATERIALS AND RESULTING PRODUCTS

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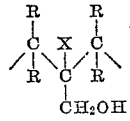
No Drawing. Filed Dec. 30, 1960, Ser. No. 79,484
13 Claims. (Cl. 117—139.5)

This invention relates to a process for treating fibrous materials. More particularly, the invention relates to a process for treating fibrous materials, such as fibers, fabrics, paper and the like, to improve properties thereof, and to the resulting products.

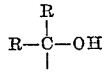
Specifically, the invention provides a new and highly efficient process for treating fibrous materials to improve their physical properties, such as strength, abrasion resistance and the like, which comprises contacting the fibrous material with a liquid medium, and preferably an aqueous medium, containing a salt of a polymeric hydroxy carboxylic acid containing a plurality of



and



units wherein X is hydrogen or



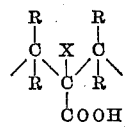
groups wherein R is hydrogen or a hydrocarbon radical, said polymeric hydroxy carboxylic acid having an intrinsic viscosity above 0.3 dl./g. and referably above 1.0 dl./g., and being preferably prepared by reacting of a polymer of an unsaturated aldehyde, such as acrolein, with a basic material and also preferably an aldehyde or ketone or material which liberates an aldehyde or ketone. The invention further provides the improved fibrous material prepared by the above process.

It is desirable to apply a sizing material to yarn, threads and filaments to improve their weaveability. The sizing material must impart fiber lay, i.e., smoothness to the fiber surface, as well as improved abrasion resistance, tensile strength and some degree of stiffness. The sizing material must also be able to be removed after the weaving and before the yarn, threads, etc. are subjected to subsequent treatment, such as dyeing. Materials used for this purpose heretofore have included starch and various cellulosic derivatives. These materials have not been too satisfactory for this application, however, as they must be used in large amounts, do not give the abrasion resistance required for many applications, are difficult to remove and the disposal of the resulting products raises a pollution problem.

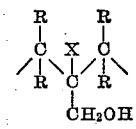
It is an object of the invention therefore to provide a new process for the treatment of fibrous materials. It is a further object to provide a new process for sizing yarn and other textile materials. It is a further object to provide a process for applying sizing material to yarn to impart fiber lay, abrasion resistance and improved tensile strength. It is a further object to provide a process for applying sizing material to yarn which is more efficient, i.e., uses less sizing agent, than conventional processes. It is a further object to provide a process for

sizing fibrous materials which permits easy removal of the sizing agent. It is a further object to provide a process for sizing fibrous materials which involves no pollution problem in disposal of the sizing material. It is a further object to provide an improved process for treatment of paper and paper products. These and other objects of the invention will be apparent from the following detailed description thereof.

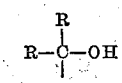
It has now been discovered that these and other objects of the invention can be accomplished by the process comprising contacting the fibrous material with a liquid medium, and preferably an aqueous medium, containing a salt of a polymeric hydroxy carboxylic acid containing a plurality of



and



units wherein X is hydrogen or



group wherein R is a hydrogen or hydrocarbon radical, said polymeric hydroxy carboxylic acid having an intrinsic viscosity above 0.3 dl./g. and preferably above 1.0 dl./g. It has been found that fibrous material treated according to the above process has excellent abrasion resistance and improved strength. Yarns and other fibers treated with the above-noted materials also have excellent fiber lay and the necessary stiffness for excellent weaveability. Surprisingly, these improved properties are obtained by the use of only very small amounts of the treating agent and in this regard the process is far superior to known treating techniques. Further advantage is also found in the fact that the treating materials may be easily removed from the fibrous material before it is used for its intended applications, and there is no pollution problem involved in disposing of the washing solution.

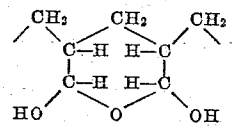
The polymeric hydroxy carboxylic acids used in making the salt sizing agents can be prepared in any suitable manner. They are preferably obtained from polymers of unsaturated aldehydes or water-soluble derivatives thereof by reacting such polymers with basic materials alone or in combination with aldehydes or ketones.

The polymers of the unsaturated aldehydes used in preparing the hydroxy carboxylic acids are the addition-type polymers obtained by polymerizing ethylenically unsaturated aldehydes through the double bonds. Examples of such unsaturated aldehydes include, among others, the alpha,beta-ethylenically unsaturated monoaldehydes, such as acrolein, and alpha and beta-substituted acroleins, such as methacrolein, alpha-ethylacrolein, alpha-butyl acrolein, alpha-chloroacrolein, beta-phenylacrolein, alpha-decylacrolein, and the like. The polymers include the homopolymers of acrolein as well as the copolymers of the aldehydes with other unsaturated materials, and preferably those containing ethylenic groups which may be contained in a $CH_2=C=$ group, such as ethylene, propylene, isobutylene, octene, vinyl acetate, vinyl propionate, vinylpyridine, styrene, vinylcyclohexane, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, acrylate esters, such as, for example, methyl methacrylate, ethyl acrylate, butyl acrylate, octyl acrylate,

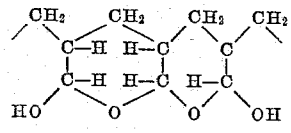
allylic compounds as allyl acetate, allyl alcohol, allyl benzoate, allyl amines and the like. These additional monomers are employed preferably only in minor amounts, and still more preferably in amounts ranging from about .5% to 45% by weight of the monomer being polymerized. Also included in the above are the conjugated diolefins, such as butadiene, isoprene, chloroprene, cyclopentadiene and the like. These are generally also used in minor amounts, such as .5% to 45% by weight of the monomer mixture.

The polymers of unsaturated aldehydes employed have high molecular weights and preferably have molecular weights ranging from about 75,000 to 2,000,000, and more preferably between 100,000 and 1,000,000, as determined by the light scattering technique. The molecular weight ranges also may be indicated by intrinsic viscosity values as these are the more easily determined. Preferred polymers are those having intrinsic viscosities (as determined on the solubilized form of the polymer) of at least 0.5 dl./g. and preferably 1.0 and 5.0. These values are determined by the conventional technique of polyelectrolyte viscosity measurements at 25° C.

The preferred polymers are those possessing a high theoretical aldehyde function, i.e., when the polymer is subjected to conventional tests for the presence of aldehyde groups (e.g., addition of hydroxylamine hydrochloride and titrated liberated H_2O with Karl Fischer reagent) the results show a high percent, e.g., above 90%, and preferably 95% to 99%, of the theoretical aldehyde groups present as such or in the hydrated form. Many of the preferred polymers have the aldehyde groups present in the hydrated form as



and some



Many of the preferred polymers are also insoluble in water and insoluble in conventional solvents, such as benzene, toluene, acetone, and the like. They may be used as such or they may be converted to the soluble form as by treatment with various materials, such as sulfur dioxide, sodium sulfite, mercaptans, alcohols and the like.

The above-described polymers may be prepared by a variety of different methods. They may be prepared, for example, by heating the acrolein with free radical catalysts, such as peroxides as benzoyl peroxide, tertiary butyl hydroperoxide, tertiary butyl perbenzoate, tertiary butyl peracetate and the like, in bulk, emulsion or suspension systems.

Conversion of the water-insoluble polymers to soluble form may be accomplished by a variety of methods. The conversion is preferably accomplished by suspending the high molecular weight polymer in an aqueous solution containing the water-solubilizing agent, such as, for example, sulfur dioxide or an alkali bisulfite as soduim bisulfite. The amount of polymer added will vary depending on the particular agent involved and concentration of the agent. In general, it is preferred to add from 1 to 50 parts of the polymer of the agent. In general, it is preferred to add from 1 to 50 parts of the polymer per 100 parts of water. The concentration of the solubilizing agent will generally vary from about 1% to about 25%. Stirring and heating may be applied to assist in the dissolution. Temperatures employed will generally vary from about 20° C. to about 90° C. Various other means, such as addition of small amounts of acid catalysts or the addition of swelling agents, such as acetone, tetrahydrofuran, etc. may also be employed in the dissolution.

High molecular weight acrolein polymers and their soluble forms which give outstanding results in the process of the invention are described and claimed in copending patent application Serial No. 859,156, filed December 14, 1959, and copending application Serial No. 859,154, filed December 14, 1959, and so much of the disclosure of these two applications relative to the polymers and derivatives and their preparation is incorporated into this application.

The preparation of some of the acrolein polymers by the above-noted method is illustrated below.

POLYMER A

100 parts of acrolein was added to 400 parts of water, to this mixture was added .271 part of potassium persulfate, .203 part of ferrous chloride tetrahydrate, 1 part of nonyl-phenol-ethylene oxide adducts as anti-coalescent agent and .4 part of disodium salt of ethylene diamine tetracetic acid. The resulting mixture was stirred for 24 hours at room temperature under atmosphere of nitrogen. During this period a white solid precipitated to the bottom. The mixture was filtered and the solid precipitate was washed with water and dried to yield 47 parts of polymer. The resulting product was a white powder polymer having an intrinsic viscosity (as determined on the sulfur dioxide solubilized form) of 1.8 di./g.

POLYMER B

100 parts of acrolein was added to 300 parts of water and to this mixture was added .272 part potassium persulfate, .203 part of ferrous choride tetrahydrate and .4 part of disodium salt of ethylene diamine tetracetic acid. The resulting mixture was stirred for 25 hours at 0° C. under an atmosphere of nitrogen. During that period a white solid precipitated to the bottom. The mixture was filtered and the solid precipitate was washed with water and dried to yield 27 parts polymer. The resulting product was a white powder polymer having an intrinsic viscosity (as determined on the sulfur dioxide solubilized form) of 2.3 dl./g.

POLYMER C

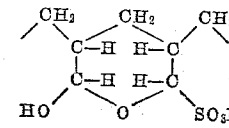
1000 parts of acrolein was added to 2000 parts of water and to this mixture was added 2.73 parts of potassium persulfate, 2.02 parts ferrous chloride tetrahydrate, 10 parts of nonylphenol-ethylene oxide condensate and 4 parts of disodium salt of ethylene diamine tetracetic acid. This mixture was stirred for 42 hours at room temperature (20° C.) under nitrogen. The resulting product was a white powder polymer having an intrinsic viscosity of 1.5.

POLYMER D

100 parts of acrolein was added to 325 parts of water and to this mixture was added 2.70 parts of potassium persulfate, 2.00 parts of ferrous chloride tetrahydrate and 4 parts of disodium salt of ethylene diamine tetracetic acid. This mixture was kept at room temperature for 6 hours with stirring and under an atmosphere of nitrogen. The resulting 46 parts product was a white powder polymer having an intrinsic viscosity of 1.02 d.l/g.

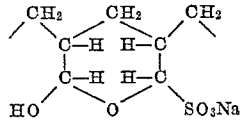
POLYMER E

10 parts of the solid Polymer A prepared as above was added to aqueous SO_2 solution and the mixture heated to 50° C. After a few minutes, the polymer dissolved to form a clear solution. Analysis indicated the polymer contained plurality of structural units



POLYMER F

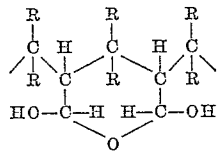
10 parts of the solid Polymer B prepared as above was added to water to form a suspension thereof. Sodium bisulfite was then added and the mixture heated to 50° C. After a few minutes, the polymer dissolved to form a clear solution. Analysis indicated the polymer contained plurality of structural units



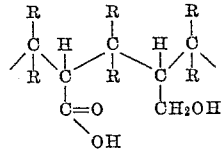
The polymeric polyhydroxy polycarboxylic acids used in making the salt sizing agents are prepared by treating and reacting the above-described acrolein polymers with a basic material with a dissociation constant greater than 2.0×10^{-5}. The basic materials used in the reaction are preferably the alkali metal hydroxides, alkaline earth metal hydroxides, strong amines, ammonium hydroxide and the like. Preferred materials to be employed are the water-soluble hydroxides and basic salts of the alkali metals, sodium, potassium and lithium and ammonium hydroxide and basic salts. The pH value of the reaction mixture is preferably between about 8 and 14. When expressed on a normality basis, it is preferred to use reaction media having a normality greater than 0.1 N and preferably between 0.5 N and 10 N.

The degree of alkalinity employed will vary depending on the degree of conversion of the aldehyde or hydrated aldehyde groups to the OH and carboxyl groups. Theoretically one mole of caustic is needed for every two aldehyde groups converted. To obtain high degree of conversions, such as 70 to 90% conversion, solutions of higher normality should be employed, while for the lower conversions, lower normality may be utilized.

As noted, the amount of hydroxyl groups and carboxyl groups present on the acid molecule will depend on the extent of reaction with the alkaline material as noted above. Preferred products have up to 90% of the aldehyde groups or hydrated groups converted to the hydroxyl and carboxyl groups. When less than 100% conversion is made, the resulting polymer will, of course, still possess the aldehyde groups or hydrated groups in the same condition as below. Particularly preferred products possess up to 40% of the aldehyde groups in the structural unit as



and the remaining groups converted to the structural units as



(wherein R is hydrogen or hydrocarbon).

The above-noted reaction with the alkaline material may be accomplished in an inert solvent medium, such as in alcohol and the like. Best results, however, are obtained when conducted in an aqueous medium.

Dilute solutions or suspensions of the polymer are preferred. The concentration of the polymer in the reaction mixture will preferably vary from about 0.01% to 5% and more preferably from 0.1% to 4%.

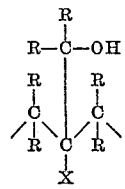
The temperature employed in the reaction will generally range from about 0° C. to as high as 60° C. Preferred temperatures range from about 15° C. to 50° C.

Atmospheric, subatmospheric or superatmospheric pressures may be utilized as desired.

In most cases, the polymers will dissolve in the alkaline medium in a few minutes and the reaction should be complete in the matter of a few hours. Reaction times generally range from about 20 minutes to about 50 hours.

The resulting hydroxy carboxylic acids will be present in the reaction mixture in the form of the alkaline salt. If this is the desired salt to be used in the treating process, the solution may be used directly in that application. If the salt is not the desired one, the salt may be converted to the acid form by precipitation with acids, such as hydrochloric acid, and then converted to the desired salt by conventional technique, or the salt may be converted directly to the other salt by conventional techniques.

A particularly outstanding and preferred group of salts to be in the process of the invention include the salts of polymeric hydroxy carboxylic acids which have the specific units



wherein X is $-CH_2OH$



or —COOH and R is hydrogen or hydrocarbon.

The polymeric hydroxy carboxylic acids used in preparing the above special salts are obtained by reacting the above-noted polymers of unsaturated aldehydes with a basic material having a dissociation constant greater than 2.0×10^{-5}, and in the presence of an aldehyde or ketone or material which liberates an aldehyde or ketone, and preferably in the presence of formaldehyde.

The basic material used in the reaction may be as described above for the simple basic reaction with the aldehyde polymer. The pH of the reaction mixture is preferably between 7.1 and 14. When expressed on a normality basis, it is preferred to use reaction media having a normality greater than 0.01 N, and preferably between 0.09 N and 2 N.

The other material employed in the reaction comprises an aldehyde or ketone or mixtures thereof. Examples of aldehyde include, among others, formaldehyde and materials liberating formaldehyde as trioxane, paraformaldehyde and the like, acetaldehyde, propionaldehyde, chloropropionaldehyde, butyraldehyde, isobutyraldehyde, valeroaldehyde, caproic aldehyde, heptoic aldehyde, acrolein, methacrolein, nicotinaldehyde, 2-pyrancarboxyaldehyde, tetrahydropyran - 2 - carboxyaldehyde, 2 - furaldehyde, crotonaldehyde, benzaldehyde, 1-naphthaldehyde, durene dialdehyde, glutaraldehyde, 1-cyclohexene-1-carboxyaldehyde, and 2,4-heptadiene-1-carboxyaldehyde. Preferred aldehydes to be used include those of the formula



wherein R is hydrogen or a hydrocarbon radical, and preferably the aliphatic, cycloaliphatic and aromatic monoaldehydes containing from 1 to 20 carbon atoms, and still more preferably 1 to 12 carbon atoms. Formaldehyde and materials which liberate formaldehyde come under special consideration as the resulting products have particularly outstanding properties for the formation of sizing agents for fibrous materials.

Other materials that may be used in place of or in admixture with the above-described aldehydes include the ketones, and preferably the monoketones, such as, for example, methyl ethyl ketone, methyl isobutyl ketone,

dimethyl ketone, diethyl ketone, dibutyl ketone, diisobutyl ketone, ethyl octyl ketone, methyl phenylketone, methyl cyclohexyl ketone, dioctyl ketone, allyl methyl ketone, methyl isopropenyl ketone, beta-chloroallyl methyl ketone, methoxymethyl butyl ketone, and the like. Preferred ketones include those of the formula

wherein R is a hydrocarbon radical. Especially preferred are the aliphatic, cycloaliphatic, aromatic monoketones containing from 3 to 20 carbon atoms, and still more preferably from 3 to 12 carbon atoms. Dialkyl ketones come under special consideration.

The degree of alkalinity employed will vary depending on the degree of conversion of the aldehyde or hydrated aldehyde groups to the OH and carboxyl groups. Theoretically one mole of caustic is needed for every two aldehyde groups converted. To obtain high degree of conversions, e.g., 70% to 90% conversions, solutions of higher normality should be employed, while for the lower normality may be utilized. Preferably from 10% to 95% of the groups are converted to the OH and carboxyl groups.

The amount of the aldehyde or ketone employed will vary depending on the degree of conversion of the hydrogen atoms on the alpha carbon atom relative to the aldehyde or hydrated aldehyde groups to the

groups. Theoretically one mole of aldehyde or ketone is needed for every unit of aldehyde in the polymer chain to be converted. Preferably from 5% to 95% of the said hydrogen are converted and still more preferably from 10% to 90% of the said hydrogen are converted and still more preferably from 10% to 90% of the said hydrogen.

The reaction may be accomplished in an aqueous medium or in an inert solvent medium, such as in alcohol and the like. Best results, however, are obtained when conducted in an aqueous medium.

Dilute solutions or suspensions of the polymer are preferred. The concentration of the polymer in the reaction mixture will preferably vary from about 0.01% to 5% and more preferably from 0.1% to 4%.

The temperature employed in the reaction will generally range from about 0° C. to as high as 60° C. Preferred temperatures range from about 15° C. to 50° C. Atmospheric, subatmospheric or superatmospheric pressures may be utilized as desired.

In most cases, the polymers will dissolve in the alkaline reaction medium in a few minutes and the reaction should be complete in the matter of a few hours. Reaction times generally vary from about 20 minutes to about 50 hours.

The desired hydroxy carboxylic acids will be present in the reaction mixture in the form of the alkaline salt. If this is the desired salt to be utilized in the treating process, the solution may be used directly in the application. If the salt is not the desired one, the salt may be converted to the acid form by the addition of acid, such as hydrochloric acid, and then converted to the desired salt by conventional techniques, or the salt may be converted to the desired salt by conventional techniques, or the salt may be converted directly to the other salt by conventional techniques.

The cationic or positive portion of the salt to be employed in the process may vary depending on the medium employed and intended application. Preferred salts include the ammonium, amine and metal salts, and particularly the alkali and alkaline earth metal salts. Examples include, among others, the sodium, potassium, lithium, ammonium, copper, zinc, magnesium, iron, cadmium, calcium, barium, and the like. Preferred metals have atomic weights from 22 to 190.

The salts are preferably prepared by treating the above-described hydroxy carboxylic acids with the desired inorganic salt or hydroxide, such as NaOH, KOH, copper sulfate, zinc sulfate, magnesium chloride, and the like, preferably in the presence of a diluent as water, alcohol and the like. The salt may then be recovered by evaporation, distillation of diluent, crystallization and the like. The salts are recovered as solids and preferably crystalline solids.

The above-described salts are applied to the fibrous material in a liquid medium. Suitable liquids include water, alcohols, mixtures of water and alcohols, ketone solvents and the like. Especially outstanding results are obtained when the salts are applied as an aqueous medium.

Other materials may be included in the treating solution, such as, polyhydric alcohols as glycerol, plasticizers, stabilizers, resins, and the like.

The application of the liquid medium containing the salt to the fibrous material may be accomplished in any suitable manner. If it is desired to apply the solution only to one surface of the material, as, for example, when it is desired to treat the back only of a fabric, the application may be effected by spraying a liquid or gas or by means of rollers, or the composition may be spread upon the surface by means of a doctor blade. The solution may also be applied locally to the material, for example, by means of printing rollers or by stencilling. When it is desired to treat both surfaces or the entire fiber, filament and the like, or if the material is to be thoroughly impregnated with the solution, the material may be dipped in the solution or run through convention-type padding rollers. The yarns, filaments, fibers, etc. may be treated in hank form or as single strands. The solution may be applied to the already formed material or may be applied just as it is being formed or immediately thereafter. It is desirable in some cases, for example, to size the fibers, filaments and the like just after they leave the spinning apparatus.

The amount of the salts to be deposited on the material varies over a wide range. In general, it is preferred to deposit from about .1% to 5% by weight of the salt on the textile material. If stiffer materials are required, the amount may go as high as 20% or higher.

If the desired amount of salt to be deposited is not obtained in one application, the solution can be applied as many times as desired in order to bring the amount of salt up to the desired level.

After the desired amount of salt has been applied, the treated material is preferably dried. This is generally accomplished by exposing the wet material to hot gas at temperatures ranging from about 40° C. to 120° C. The period of drying will depend largely on the amount of pick-up permitted during the application of the solution and the concentration of the salt solution. In most instances, drying periods of from about 1 minute to 30 minutes should be sufficient.

The sizing prepared from the water-soluble salts, such as the sodium salt, may be removed after it has served its purpose by simply scouring or washing the treated material with water or aqueous soap solution.

The above-described process may be utilized for the treatment of any fibrous material. This includes textile material, such as woven fabrics, non-woven fabrics, threads, yarn, cord, and string, paper, and the like. These materials may be prepared from natural or synthetic materials, such as cotton, linen, natural silk and artificial silk, such as silk obtained from cellulose acetate or other organic esters or ethers of cellulose, rayons, jute, hemp, animal fibers, such as wood, hair, and the like as well as synthetic materials which include, among others, those prepared from acrylonitrile (Orlon—100% acrylonitrile polymer), vinylidene cyanide polymers, polyamides (nylon—superpolyamide), polyester-polyamides, cellulose esters and ethers, and polymers prepared from corn protein and formaldehyde (zein). This includes the homopolymers as well as copolymers and terpolymers, such as, for example, Acrilan (85% acrylonitrile and 15% vinyl acetate), Dynel (60% vinyl chloride and 40%

acrylonitrile). The fibrous material may be colorless or may be dyed, printed or otherwise colored to the desired shade.

The material treated as noted above has many improved properties. The fibers, yarn and the like, prepared from materials as cotton and other cellulosic materials have improved warp sizing properties, such as strength and abrasion resistance. Other textile materials have improved dry strengths, resistance to shrinkage and the like. The paper has better dry strength, fold endurance and abrasion resistance.

The products treated as above may be utilized for any of the conventional applications, such as in the manufacture of dresses, drapes, upholsteries, shoe fabrics, carpets, coats, shirts and the like.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific conditions or reactants cited therein. Unless otherwise specified, parts described in the examples are parts by weight.

Example I

The example illustrates the use of a sodium salt of a polymeric hydroxyl carboxylic acid prepared from polyacrolein (intrinsic viscosity of about 1.6 dl./g.), sodium hydroxide and formaldehyde, as a sizing agent for cotton yarn.

A polyhydroxy carboxylic acid was prepared from a solid polyacrolein having an intrinsic viscosity of 1.6 dl./g., by treatment with sodium hydroxide and formaldehyde. The product had the following properties: OH value 0.778 eq./100 g., acidity of 0.4 eq./100 g. and carbonyl value of 0.354 eq./100 g. The sodium salt was prepared by treating the resulting acid with sodium hydroxide.

A 2% solution of the sodium salt of the above-described acid was used to impregnate cotton yarn by passing the yarn into and through the water solution. The yarn was then dried at 100° C. for 0.5 minute. The treated yarn was then tested for force at break, elongation at break and abrasion resistance (as indicated by the number of cycles of wear before break). The results are shown below in comparison to the results obtained with a commercial sizing agent, and a control:

Warp Sizing Material	Force at Break	Elongation at Break, Percent	Abrasion in Cycles
Sodium salt of polymer produced above	574	8	2,893
Commercial material (5% oxidized starch)	586	7.9	1,356
Control	515	7.8	125

From the above, it is apparent that the new sodium salt gives an unexpected improvement in the resistance to abrasion.

Further advantage is also found in the fact that the new sodium salts can be easily removed from the yarn by washing while the commercial material was quite difficult to remove.

Example II

A polyhydroxy carboxylic acid was prepared as follows: 415 parts of a polyacrolein having an intrinsic viscosity of 1.6 dl./g. and containing 88.5% water was mixed with 400 parts of water and 42 parts of 37% formalin. 2000 parts of 1 N NaOH was added to this solution at 5° C. with stirring under nitrogen. The mixture was allowed to stand at room temperature and then made acid. A white granular polymer precipitated. The polymer identified as a polyhydroxy polycarboxylic acid had an OH value of 1.404 eq./100 g., acid value of 0.39 eq./100 g. and a carbonyl value of 0.33 eq./100 g. A sodium salt of the acid was prepared by treating a water solution of the above acid with sodium hydroxide.

A 2% solution of the sodium salt of the above-described acid was used to impregnate cotton yarn by passing the yarn into and through the water solution. The yarn was then dried at 100° C. for 0.5 minutes. The yarn had a force at break of 569, an elongation at break of 8% and an abrasion cycle value of 2275.

Example III

This example illustrates the use of a salt of a hydroxy carboxylic acid prepared from a polyacrolein by using caustic alone.

12.0 parts of polyacrolein having an intrinsic viscosity of 1.0 dl./g. (Polymer D above) was stirred with 550 parts of water and 550 parts of 1 N NaOH added thereto. After stirring several hours, the solution was neutralized and filtered. The resulting product was identified as a polymeric hydroxy carboxylic acid wherein about 80% of the aldehyde groups had been converted to OH and COOH groups. A sodium salt was prepared by treating the acid in water solution with sodium hydroxide.

A 2% solution of the sodium salt of the above-described acid containing glycerol was used to impregnate cotton yarn as in Example I. The resulting yarn had a break at force of 658, and abrasion cycle value of 1817. A control sample had a break at force of 515 and an abrasion cycle of 125.

Example IV

Examples I and II are repeated with the exception that the polyacrolein used in the initial reaction had an intrinsic viscosity of 1.0 dl./g. and 2.8 dl./g. Related results are obtained.

Example V

Examples I and II are repeated with the exception that the hydroxy carboxylic acid is employed in the preparation of an ammonium salt. This salt also gave very high abrasion cycle values when applied as a warp sizing agent for cotton yarn.

Example VI

75 parts of polyacrolein having an intrinsic viscosity of 1.6 dl./g. and containing 85.5% water was stirred with 50 parts of water and 25 parts of 37% formalin solution. 1500 parts of 0.2 N NaOH was added to this solution at 5° C. under nitrogen with stirring. The mixture was then made acid by addition of 5 N sulfuric acid. A white granular polymer precipitated. The polymer identified as a polyhydroxy polycarboxylic acid had an intrinsic viscosity of about 1.6 dl./g., and OH value of 1.258 eq./100 g., acidity of 0.4 eq./100 g. and a carbonyl value of 0.416 eq./100 g.

Sodium, potassium and ammonium salts prepared from the above-described hydroxy carboxylic acid polymer are prepared and used as warp sizing agents for cotton yarn as shown in Example I. Related results are obtained.

Example VII

160 parts of polyacrolein having an intrinsic viscosity of 1.5 dl./g. and containing 85.5% water mixed with 150 parts of water and 8 parts of 37% formalin. To 310 parts of this mixture was added 800 parts of 1 N TiOH at 5° C. under nitrogen with stirring. This mixture was then allowed to stand at room temperature with stirring. After standing several days, the mixture was diluted with water and made acid to pH of 2.5 by addition of 5 N sulfuric acid. A white granular polymer precipitated. The polymer identified as a polyhydroxy polycarboxylic acid had an intrinsic viscosity of about 1.5 dl./g., an OH value of 0.8 eq./100 g., an acidity of .4 eq./100 g. and a carbonyl value of 0.3 eq./100 g.

A sodium salt of the above-described polymer was prepared by the addition of sodium hydroxide. A 2% solution of the salt was used to impregnate cotton yarn by

conventional padding technique. The yarn was dried and then tested as in Example I. The yarn had a force at break of 569, an elongation at break of 8% and an abrasion cycle value of 3647.

Example VIII

80 parts of a polyacrolein having an intrinsic viscosity of 1.6 dl./g. and containing 82% water was mixed with 80 parts of a 37% formalin solution. To this mixture was added 2000 parts of an 0.1 N NaOH solution under nitrogen with stirring. The mixture was stirred at room temperature for several days. The mixture was then filtered and made acid by addition of 5 N sulfuric acid. A white granular polymer precipitated which was identified as a polymeric hydroxy carboxylic acid having an intrinsic viscosity of about 1.6 dl./g., an OH value of 0.84 eq./100 g., acidity of 0.3 eq./100 g., and carbonyl value of 0.600 eq./100 g.

Sodium, potassium and ammonium salts are prepared from the above-described polymer and used as warp sizing agents for cotton yarn as shown in Example I. Related results are obtained.

Example IX

800 parts of polyacrolein having an intrinsic viscosity of 1.6 dl./g. and containing 85% water was mixed with 800 parts of water and 160 parts of 37% formalin. To this mixture was added 5000 parts of 0.5 NaOH at 5° C. under nitrogen with stirring. The mixture was stirred at room temperature for several days. The mixture was then made acid by addition of 5 N sulfuric acid. A white granular polymer precipitated. The polymer was identified as a polymeric hydroxy carboxylic acid.

A sodium salt of the above-described hydroxy carboxylic acid was prepared by the addition of sodium hydroxide. A 2% solution of the salt was prepared to impregnate cotton yarn by conventional padding technique. The yarn was dried and tested as in Example I. The yarn had an abrasion cycle value of 2633.

Example X

This example illustrates the preparation of a sodium salt of polymeric hydroxy carboxylic acid from a copolymer of acrolein and ethyl acrylate having an intrinsic viscosity of 1.0 dl./g., sodium hydroxide and formaldehyde, and its use for treating yarn.

84 parts of a 70:30 copolymer of acrolein and ethyl acrylate containing 55% water and having an intrinsic viscosity of 1.7 dl./g. was mixed with 300 parts of water and 40 parts of 37% formalin. To 87 parts of this mixture was added 1500 parts of 0.5 N NaOH at 5° C. under nitrogen. The mixture was then allowed to stand at room temperature with stirring. The mixture after 2 days was made acid by adding 5 N sulfuric acid. A white granular polymer precipitated. The polymer was identified as hydroxy carboxylic acid having an OH value of 0.726 eq./100 g., acidity of 0.55 eq./100 g. and a carboxyl value of 0.241 eq./100 g.

Sodium, potassium and ammonium salts are prepared from the above-described polymer and used as warp sizing agents for cotton yarn as shown in Example I. Related results are obtained.

Example XI

Example IX was repeated with the exception that the copolymer employed was as follows: copolymer of 50 parts acrolein and 50 parts methyl acrylate; copolymer of 70 parts acrolein and 30 parts acrylonitrile; and a copolymer of 70 parts of acrolein and 30 parts of methyl ethyl ketone. Related results are obtained.

Example XII

Examples I to IV and X are repeated with the exception that benzaldehyde is used in place of formaldehyde. Related results are obtained.

Example XIII

Examples I to IV and X are repeated with the exception that methyl ethyl ketone and ethyl butyl ketone are used in place of formaldehyde sodium salts of the polymeric hydroxy carboxylic acids can be used as sizing agents for cotton yarn and paper.

Example XIV

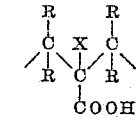
Examples I to XI are repeated with the exception that the solutions are applied to cotton fabrics. Related results are obtained.

Example XV

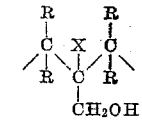
Examples I to X are repeated with the exception that the solutions are applied to rayon, nylon, Orlon and Dacron fabrics. Related results are obtained.

We claim as our invention:

1. A process for treating fibrous textile materials to improve their properties which comprises contacting the fibrous materials with a liquid medium containing a salt of a polymeric hydroxy carboxylic acid which contains a plurality of



and



units wherein X is a member of the group consisting of hydrogen and R—C—OH groups, wherein R is a member of the group consisting of hydrogen and hydrocarbon radicals, said polymeric hydroxy carboxylic acid having an intrinsic viscosity above about 0.3 dl./g.

2. A process for treating textile material which comprises contacting the material with an aqueous medium containing a water-soluble salt of a polymeric hydroxy carboxylic acid, which polymeric acid has an intrinsic viscosity between 0.5 dl./g. and 5.0 dl./g. and has been obtained by treating and reacting a polymer of acrolein with a basic material having a dissociation constant greater than 2.0×10^{15}, said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein, having an intrinsic viscosity between 0.5 dl./g. and 5.0 dl./g. and possessing when prepared at least 95% of the theoretical aldehyde function as determined by addition of hydroxylamine hydrochloride and titrating with Karl Fischer reageant the liberated water, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

3. A process as in claim 2 wherein the textile material is cotton yarn.

4. A process as in claim 2 wherein the textile material is rayon.

5. A process as in claim 2 wherein the textile material is nylon.

6. A process as in claim 2 wherein the textile material is polyacrylonitrile.

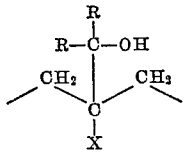
7. A process as in claim 2 wherein the water-soluble salt is a sodium salt.

8. A process as in claim 2 wherein the water-soluble salt is an ammonium salt.

9. A process for warp sizing of cotton fibers which comprises impregnating the fibers with an aqueous medium of a water-soluble salt of a polymeric hydroxy polycarboxylic acid obtained by reacting a polymer of acrolein with caustic, said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein, having an intrinsic viscosity of at least 0.3 dl./g. and possessing when prepared at least 95% of the theoretical aldehyde function as determined

by addition of hydroxylamine hydrochloride and titrating with Karl Fischer reagent the liberated water, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

10. A process for treating textile material which comprises contacting the material with an aqueous medium containing a water-soluble salt of a polymeric hydroxy carboxylic acid groups having a plurality of structural units.

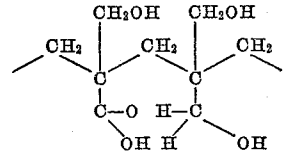


units wherein R is a member of the group consisting of hydrogen and hydrocarbon radicals and X is a member of the group consisting of $-CH_2OH$,



and —COOH, said polymeric carboxylic acid having an intrinsic viscosity above about 0.5 dl./g.

11. A process for warp sizing of cotton fibers which comprises impregnating the fibers with an aqueous medium containing a water-soluble metal salt of a polymeric carboxylic acid containing a plurality of units



which polymer has an intrinsic viscosity above 0.90 dl./g.

12. A process as in claim 11 wherein the salt is a sodium salt.

13. A process as in claim 11 wherein the salt is an ammonium salt.

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