The present invention relates to the permanent sizing of textile warp yarns, particularly colored cellulose acetate warp yarns, and to the production of loom-finished fabrics, that is, fabrics which require no wet processing after removal from the loom.

It has been proposed heretofore to treat cotton and rayon yarns with aqueous solutions of alkali metal or ammonium salts of copolymers of substantially equimolecular proportions of styrene or vinyl acetate and maleic acid or maleic anhydride to provide a finish on such yarns. However, the finish provided by the alkali metal salts of such copolymers is water-soluble and is readily removed from the yarn by washing in water. While this result is desirable in certain applications, the yarns are not suitable for producing loom-finished fabrics because the finish is not permanent. The finish provided by the ammonium salts of the above copolymers is sufficiently permanent to enable the yarns treated with such ammonium salts to be used in the preparation of loom-finished fabrics. Unfortunately, however, loom-finished fabrics prepared from yarns finished with such ammonium salts are not entirely satisfactory since the application, whether accidental or otherwise, of droplets of water on such fabrics results in the formation of noticeable spots, often termed “water-spots” in the trade. Consequently, the use of yarns finished with the ammonium salts of the above copolymers in the preparation of loom-finished fabrics has not been accepted to any appreciable extent by the trade.

It has also been proposed heretofore to modify aqueous solutions of ammonium salts of copolymers of substantially equimolecular proportions of styrene and maleic anhydride with cross-linking materials such as formaldehyde, alkylene polyamines, urea-formaldehyde or melamine-formaldehyde. Such modified solutions are then applied to yarns and heated at temperatures of about 250 to 300°F to obtain a reaction between the ammonium salt of such copolymer and the cross-linking material. Such heating is necessary and requires an additional heating step because the desired temperatures and duration of heating cannot be attained in a conventional warp sizing slasher. This means that the treated yarns must be given an additional processing before weaving and this increases the cost of production considerably. Moreover, in the case of thermoplastic yarns such as cellulose acetate yarns, the additional heating required may cause detrimental deformation of the yarn due to plastic flow. Further, fabrics prepared from yarns sized with such materials also show water-spots when droplets of water are applied to the fabric.

In accordance with the present invention, it is possible to permanently size textile warp yarns, particularly colored cellulose acetate warp yarns, with a single sizing agent to provide yarns which may be used directly in the preparation of loom-finished fabrics without the additional step required in the process described in the preceding paragraph. Moreover, the fabric thus obtained does not “water-spot” to any appreciable extent.

It is, accordingly, one object of this invention to provide an improved process of permanently sizing textile warp yarns, particularly colored cellulose acetate yarns.

It is a further object of this invention to provide permanently sized textile warp yarns, particularly permanently sized colored cellulose acetate warp yarns, which are suitable for the production of commercially acceptable loom-finished fabrics.

It is a further object of this invention to provide improved processes of preparing commercially acceptable loom-finished fabrics.

It is a further object of this invention to provide loom-finished fabrics which do not spot to any detrimental extent on the application thereto of droplets of water.

Still further objects and advantages of this invention will become apparent from the following description and the appended claims.

The objects of this invention are attained, in general, by first coating textile warp yarns, preferably colored cellulose acetate warp yarns, with an aqueous solution of a water-soluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carbonyl group and from 3 to 8 carbon atoms, for example, crotonic acid or an alkyl half ester of maleic acid having from 1 to 4 carbon atoms in the alkyl group, which solution is free of cross-linking agents for such ammonium salt, or which is free of bifunctional compounds which react with such ammonium salt to form cross-linked polymers. The treated yarns are next dried, as, for example, by passing them over heated drying cans in a conventional slasher, and then are taken up on a suitable device such as a beam for use directly as a warp in a power loom. In the loom the sized yarns, thus obtained, are woven with an unsized filling yarn to provide a loom-finished fabric, that is, a fabric which is used directly for apparel or other purposes without any subsequent wet processing operations. The size on the warp yarns of the fabric is substantially permanent, that is, it is not materially affected by mild launderings or ordinary dry cleanings.

A large variety of textile warp yarns may be permanently sized according to the processes of this invention, but since the present invention relates primarily to the production of loom-finished fabrics which by their nature are not subjected to subsequent wet processing operations the processes described herein are directed primarily to the permanent sizing of colored textile warp yarns which require no coloring or dyeing procedure after the production of the loom-finished fabric. Such colored textile warp yarns may be obtained in various ways, but those which are most suitable are the synthetic yarns produced by spinning a fiber-forming solution to which coloring matter has been added prior to extrusion of the yarn. As examples of such yarns may be mentioned colored cellulose acetate yarns, colored polyacrylonitrile yarns, colored nylon yarns and the like. The nylon yarns may be prepared from synthetic fiber-forming linear polyamides such as those described in U. S. Patent No. 2,071,250, U. S. Patent No. 2,130,523 and U. S. Patent No. 2,130,948.

The nylon yarns prepared from polyhexamethyleneadipamide are preferred over other nylon yarns for use according to the present invention. However, since the sizing agent of this invention has exceptional adhesion when applied to cellulose acetate warp yarns, it is preferred to employ colored cellulose acetate warp yarns, in the sizing process of this invention.

The sizing agent of this invention is suitably prepared by stirring an aqueous ammonia-soluble copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carbonyl group and from 3 to 8 carbon atoms, in an aqueous solution of ammonia until a solution of the ammonium salt of the copolymer is obtained. The concentration of such ammonium salt in solution depends on the amount of copolymer employed,
the molecular weight of the copolymer and the concentration of the ammonia solution. In general, satisfactory sizing solutions contain from about 1 to 10% by weight of the water-soluble ammonium salt of the copolymer. The copolymer from which the sizing agent is prepared may be made by copolymerizing from 95 to 99 mol percent of vinyl acetate with from 5 to 1 mol percent of a large variety of ethylenically unsaturated aliphatic carboxylic compounds having one carboxyl group and from 3 to 8 carbon atoms and which copolymerize with vinyl acetate. As examples of such carboxylic compounds may be mentioned the ethylenically unsaturated aliphatic monocarboxylic acids such as alkenic monocarboxylic acids having from 3 to 6 carbon atoms, as, for example, acrylic acid, butenics such as crotonic acid, isocrotonic acid, methacrylic acid, and vinylacetic and pentenic acids such as flicic and angelic acids. In general, the ethylenically unsaturated aliphatic monocarboxylic acids of the general formula, \( \text{C}_n\text{H}_{2n-2}\text{O}_2 \), where \( n \) is a whole number from 3 to 6, and which are polymerizable with vinyl acetate may be employed to prepare the copolymer. Of the above group of acids crotonic acid is preferred because it is available commercially and copolymerizes with vinyl acetate to give copolymers from which superior sizing agents for use in this invention are obtained.

As further examples of the carboxylic compounds which may be used with vinyl acetate to prepare the copolymer may be mentioned the half esters of ethylenically unsaturated monocarboxylic acids polymerizable with vinyl acetate and having from 5 to 8 carbon atoms, and preferably the alkyl half esters of such acids. As examples of such half esters may be mentioned the alkyl half esters of maleic acid in which the alkyl group contains from 1 to 4 carbon atoms, such as methyl, ethyl and propyl maleate; the alkyl half esters of fumaric acid in which the alkyl group contains from 1 to 4 carbon atoms, such as methyl acid fumarate and secondary butyl acid fumarate; the alkyl half esters of citraconic acid in which the alkyl group contains from 1 to 3 carbon atoms, such as methyl acid citraconate; alkyl half esters of chlormaleic acid in which the alkyl group contains from 1 to 4 carbon atoms, such as ethyl and butyl acid chlormalates; and alkyl half esters of itaconic acid in which the alkyl group contains from 1 to 3 carbon atoms, such as methyl and butyl acid itaconates, and the like. These esters, with the exception of the alkyl and itaconates, are represented generally by the structural formula:

![Structural formula image]

where \( R \) is an alkyl group having from 1 to 4 carbon atoms, \( X \) is hydrogen, halogen (preferably chlorine) or an alkyl group having at most a number of carbon atoms such that the total number of carbon atoms in the ester does not exceed 8, and where \( X_1 \) is the same as \( X \) or is preferably hydrogen when \( X \) is other than hydrogen. It is to be understood that the foregoing structural formula for the esters is intended to include the cis- and trans-forms of the esters. Of the above esters the alkyl half esters of maleic acid are preferred. Of the alkyl half esters of maleic acid, the methyl half ester of maleic acid is preferred.

The mol ratio of vinyl acetate to the ethylenically unsaturated carboxylic compound in the copolymer is critical for the sizing agents of this invention. For example, if the copolymer contains less than 1 mol percent of the carboxylic compound, the copolymer is not sufficiently soluble in aqueous ammonia solutions to be useful as a sizing agent. On the other hand, if the copolymer contains more than 5 mol percent of the carboxylic compound, the ammonium salt thereof does not provide a size coating which is sufficiently permanent or which is sufficiently resistant to spotting. Copolymers from the standpoint of proportions of ingredients are the copolymers of 96 to 98 mol percent of vinyl acetate and 2 to 4 mol percent of the ethylenically unsaturated carboxylic compound. The preferred copolymers of this invention from the standpoint of ingredients employed are the copolymers of vinyl acetate and crotonic acid, the copolymers of vinyl acetate and alkyl half esters of maleic acid in which the alkyl group contains from 1 to 4 carbon atoms, more particularly methyl acid maleate, and the copolymers of vinyl acetate, crotonic acid and alkyl half esters of maleic acid in which the alkyl group contains from 1 to 4 carbon atoms, more particularly methyl acid maleate.

In carrying out the copolymerization of vinyl acetate and the ethylenically unsaturated aliphatic carboxylic compound a suitable procedure comprises adding vinyl acetate monomer and the carboxylic compound in the proportions hereinafter specified to an aqueous solution, preferably having a pH of 4 to 7, in the presence of about 0.3 to 3.5%, based on the monomers, of a copolymerization catalyst, preferably an oil-soluble peroxide catalyst such as benzoyl peroxide, and a protective colloid suspending agent such as a water-soluble polyvinyl alcohol. The aqueous solution is preferably heated to 55° C. prior to the addition of the monomers and is maintained at the reflux temperature at atmospheric pressure after the addition of monomers. The aqueous solution is also stirred constantly throughout the polymerization. After the polymerization mixture contains 5% or less of unreacted monomers, the mixture is allowed to cool and the copolymer is separated from the aqueous phase by decantation, filtration or centrifugation, preferably by filtration, and then dried.

In carrying out the sizing processes of this invention the textile warp yarn is first coated with an aqueous solution of a water-soluble ammonium salt of the copolymer. This may be accomplished in various ways, but is most suitably carried out by passing the yarn through the solution which is contained in the size box of a conventional slasher. After the yarn is coated with the solution, it is preferably passed between squeeze rolls in order to insure the application of a substantially uniform coating to the yarn, and also to obtain penetration of the ammonium salt of the copolymer into the body of the yarn. The yarn is next dried and this is most suitably accomplished by passing the coated yarn over a plurality of heated drying cans of the type used in a conventional slasher. During the drying operation, the yarns are heated at temperatures above 130° F., usually between about 150 and 220° F., and the temperatures used preferably should not exceed 230° F. The dried yarns may contain up to 15% by weight of moisture.

Since the ammonium salt of the copolymer becomes water-insoluble on mere drying or further heating of the yarn is necessary or desirable. The exact mechanism by which the water-soluble ammonium salt of the copolymer becomes water-insoluble on drying of the yarns is not known, but it is believed that the ammonium salt either loses sufficient ammonium to become water-insoluble or else reverts or condenses with itself to form a water-insoluble material. Irrespective of any theory, however, a water-insoluble product is formed on the yarn and such product may be properly termed a water-insoluble ammonium salt of the copolymer. Such product has a solubility of less than 0.01, usually between 0.001 and 0.005, parts by weight per 100 parts of water. The sized and dried yarn is next taken up on a beam or other suitable device and is now ready for direct use as a warp yarn in a power loom for weaving fabrics. From the standpoint of practical considerations the present invention is most applicable to the sizing of a plurality of yarn ends sufficient to fill an entire beam which
is used directly in a power loom as a supply source of warp yarns for weaving a fabric.

As is mentioned previously herein, the sizing solution contains from about 1 to 10% by weight of the water-soluble ammonium salt of the copolymer. Of the sizing solution with the procedure described in the preceding paragraph, it is possible to apply to the warp yarn from about 1 to 10% by weight of the ammonium salt of the copolymer, based on the dry weight of the yarn. However, it is preferred to adjust the concentration of the sizing solution and to control by means of squeeze rolls, the amount of solution pick-up by the yarn, so that from about 2 to 6% by weight of the ammonium salt of the copolymer, based on the dry yarn, is deposited on the yarn. As is indicated previously herein, the solution of the ammonium salt of the copolymer should be free of cross-linking agents for the ammonium salt of the copolymer, or should be free of bifunctional compounds which react with the ammonium salt of the copolymer to form cross-linked polymers. Thus the solution should be free of aldehydes and bifunctional compounds which contain at least two reactive groups selected from the following: amino, amido, imido and hydroxyl. However, the sizing solution may contain various sizing adjuvants which do not cross-link the ammonium salt of the copolymer. For example, the solution may contain monofunctional wetting agents which contain sulfonate or sulfate groups as, for example, sulfonated or sulfonated water at 160° F., after which 45 pounds of a granular copolymer of 97 mol percent of vinyl acetate and 3 mol percent of crotonic acid were added with stirring and stirring was continued for 15 minutes while maintaining the solution at 160° F. Finally five (5) pounds of sulfated coconut oil were added and the solution was diluted with water until the total volume of solution was 100 gallons. This solution was then charged to a size box of a commercial size slasher and was maintained at a temperature of 120° F. during the sizing operation.

Six thousand six hundred and forty eight ends of 100 filament -26 denier Navy blue cellulose acetate continuous filament yarns having an S-twist of 2 turns per inch were drawn through the size solution, as prepared above, at the rate of 40 yards per minute and then passed between squeeze rolls adjusted to give a solution pick-up of about 50% based on the dry yarn. The wet yarns were then passed over 5 rotating drying cans arranged in tandem, which cans were maintained at temperatures of 160° F., 170° F., 180 F., 200 F. and 160° F., respectively, to dry the yarns, after which the yarns were passed over another rotating can at a temperature of about 60° F. and finally taken up on a beam. One thousand yards of yarn were successfully sized without any foaming of the size solution or accumulation of size on the drying cans. The yarns were well sized and there was no tendency for the size to flake off of the yarns.

The sized yarns were woven on a power loom into a 144 x 60 taffeta using unsized 130 denier continuous filament cellulose acetate yarns as filling yarns during weaving. Weaving was carried at a temperature of about 80° F. and at a relative humidity of 65% and the weaving efficiency of the sized yarns was excellent, there being no appreciable tendency for the size to shed during the weaving operation. The resulting fabric showed some stiffness in the warp direction only and did not spot to any appreciable extent when sprinkled with water and allowed to dry. The fabric required no wet post-treatment and the size on the warp yarns thereof was permanent to mild washing and ordinary dry cleaning.

What is claimed is:

1. A process of sizing textile warp yarns to prepare them for weaving which comprises applying to said yarns an aqueous solution of a water-soluble amphoteric ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl...
group and from 3 to 8 carbon atoms and thereafter drying said yarns at a temperature above 130° F. but not in excess of 230° F.

2. A process according to claim 1, but further characterized in that the copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of crotonic acid.

3. A process according to claim 1, but further characterized in that the copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and from 4 to 2 mol percent of vinyl half ester of maleic acid in which the alkyl group contains from 1 to 4 carbon atoms.

4. A process of sizing cellulose acetate warp yarns to prepare them for weaving which comprises applying to colored cellulose acetate warp yarns an aqueous solution of a water-soluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms, said solution being supplied in an amount sufficient to deposit from 1 to 10% by weight of said salt, based on the dry yarn weight, and thereafter drying said yarns at a temperature above 130° F. but not in excess of 230° F.

5. A process according to claim 4, but further characterized in that said copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and from 4 to 2 mol percent of crotonic acid.

6. A process according to claim 4, but further characterized in that said copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and from 4 to 2 mol percent of an alkyl acid maleate in which the alkyl group contains from 1 to 4 carbon atoms.

7. A process of sizing cellulose acetate warp yarns to prepare them for weaving which consists in the steps of applying to colored cellulose acetate warp yarns an aqueous solution of 1 to 10% by weight of water-soluble ammonium salt of a copolymer of 96 to 98 mol percent of vinyl acetate and from 4 to 2 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms, drying said yarns at a temperature above 130° F. but not in excess of 230° F. and then taking up said yarns on a beam.

8. A textile warp yarn sized with a water-insoluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and from 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms.

9. A colored cellulose acetate warp yarn sized with from 1 to 10% by weight, based on the dry yarn weight, of a water-insoluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms.

10. A warp yarn as in claim 9, but further characterized in that the copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of crotonic acid.

11. A warp yarn as in claim 9, but further characterized in that the copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of an alkyl acid maleate in which the alkyl group contains from 1 to 4 carbon atoms.

12. A process of preparing loom-finished fabrics which comprises applying to colored warp textile yarns an aqueous solution of a water-soluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms, drying said yarns at a temperature above 130° F. but not in excess of 230° F. and thereafter weaving said yarns in a loom in combination with an unsized filling yarn.

13. A process of preparing loom-finished fabrics which are resistant to water spotting which comprises applying to colored cellulose acetate warp yarns an aqueous solution of from 1 to 10% by weight of a water-soluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms, drying said yarns at a temperature above 130° F. but not in excess of 230° F. and thereafter weaving said yarns in a power loom in combination with an unsized filling yarn.

14. A process according to claim 13, but further characterized in that said copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of crotonic acid.

15. A process according to claim 13, but further characterized in that said copolymer is a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of an alkyl acid maleate in which the alkyl group contains from 1 to 4 carbon atoms.

16. A process of preparing loom-finished fabrics which are resistant to water spotting which comprises applying to colored cellulose acetate warp yarns an aqueous solution of a water-soluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 4 to 2 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms, said solution being applied in an amount sufficient to deposit from 1 to 10% of said salt, based on the dry yarn weight, drying said yarns to a moisture content of up to 15% at a temperature above 130° F. but not in excess of 230° F., combing said yarns on a beam, transferring the beam of yarns to a power loom and thereafter weaving said yarns with an unsized filling yarn in said loom, whereby the resulting fabric requires no wet processing operations.

17. A loom finished fabric composed of unsized filling yarns and colored textile warp yarns sized with a water-insoluble ammonium salt of a copolymer of 95 to 99 mol percent of vinyl acetate and 5 to 1 mol percent of an ethylenically unsaturated aliphatic carboxylic compound having only one carboxyl group and from 3 to 8 carbon atoms.

18. A loom-finished fabric composed of unsized filling yarns and colored cellulose acetate warp yarns sized with from 1 to 10% by weight, based on the dry weight of said warp yarns, of a water-insoluble ammonium salt of a copolymer of 96 to 98 mol percent of vinyl acetate and 4 to 2 mol percent of crotonic acid.

19. A loom-finished fabric composed of unsized filling yarns and colored cellulose acetate warp yarns sized with from 1 to 10% by weight, based on the dry weight of said warp yarns, of a water-insoluble ammonium salt of a copolymer of 96 to 99 mol percent of vinyl acetate and 4 to 2 mol percent of an alkyl acid maleate in which the alkyl group contains from 1 to 4 carbon atoms.

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