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PROCESS FOR SIZING ACRYLIC YARNS

Carlyle G. Caldwell, North Plainfield, Otto B. Wurzburg, Plainfield, and Louis D. Fitzgerald, Scotch Plains, N. J., assignors to National Starch Products Inc., New York, N. Y., a corporation of Delaware

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This invention relates to a method for sizing fibers and filaments composed predominantly of acrylic polymers. Examples of such fibers and filaments are those sold under the trade names "Orlon" (E. I. du Pont de Nemours & Co., Delaware), and "Acrilan" (Chemstrand Corporation, Pennsylvania). It is an object of our invention to devise a means for using starches as effective sizing materials for polyacrylic yarns.

It has long been standard practice, in the case of cotton and other natural fibers, to size the yarn by immersion in aqueous dispersions of starches, prior to weaving. This sizing operation (referred to as warp sizing) is necessary in order to help bind the individual fibers to one another in the yarn, and to strengthen the fibers so as to reduce the occurrence of yarn breakage during the subsequent weaving process. Starches have been found to be by far the most efficient and economical materials for the warp sizing of natural yarns.

With the advent of synthetic fibers and filaments, the selection of a suitable warp sizing material has frequently raised serious problems. Starches, used in the ordinary manner, have not proved to be satisfactory for many of these synthetics. Thus, in the case of the above mentioned polyacrylic fibers and filaments, starches do not appear to have a sufficient affinity for the fibers to permit their effective use (it should be pointed out that wherever we refer to "fibers" in this application, we use the term broadly so as to include filaments as well). Without proper warp sizing, the subsequent weaving of fabrics from the polyacrylic yarns is often attended by serious operating difficulties. This has led to the use, of necessity, of expensive and only partly effective sizing materials such as polyvinyl alcohol, polyacrylic acid and other synthetics.

We have now discovered a method whereby relatively inexpensive starches may be used to size polyacrylic yarns, in a most effective and efficient manner.

Our method comprises the use of a starch, preferably a starch derivative containing free acidic groups (or the salt of such a derivative), together with a salt of a metal selected from the group stannic, stannous, ceric, chromic, chromous, bismuth, and cuprous salts (the latter being formed by reacting a cupric salt with a reducing agent in situ).

Examples of suitable salts for our process include cupric chloride, cupric acetate, cupric ammonium chloride, cupric bromide, cupric nitrate and cupric sulfate (these being used in conjunction with a reducing agent to achieve the corresponding cuprous salts); also stannic chloride, stannous chloride, ceric sulfate, bismuth nitrate and chromic chloride. The particular anion chosen is not critical, and other suitable salts will be apparent to those in the art.

As the starch in our process, we may use starch derived from any vegetable source, including corn, potato, waxy maize, sago, wheat, tapioca, rice and sweet potato. We prefer that the starch be in the form of a derivative

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containing free acidic groups (in practice these would most ordinarily be carboxylic and/or sulfonic groups) or the salts of these groups. Thus, starches which have been converted with oxidizing agents such as chlorine, hypochlorites, or peroxides, to the thinner-boiling forms, known in the trade as oxidized starches, are suitable. Even more preferable are starches which have been reacted in alkaline media with organic acid anhydrides, such as maleic anhydride (as described in U. S. Patent No. 2,461,139) to form mono-esters containing the salts of carboxylic groups; or the products formed by reacting mono-esters of starch and unsaturated anhydrides such as maleic anhydride with bisulfites (as described in co-pending application, Serial No. 756,106, filed June 20, 1947). It will be noted that the starch derivatives listed above contain free acidic groups (carboxylic, sulfuric or sulfonic), or the salts of such groups. The acidic groups are naturally in the form of their salts in those cases where the reaction producing the starch derivative took place in an alkaline medium (i. e., COONa , COONH_4 , SO_3Na , etc.).

As the reducing agent, to be used in conjunction with salts such as copper sulfate, any chemical capable of reducing Cu^{++} to Cu^+ is suitable. Examples of such materials include hydroxylamine sulfate and sodium formaldehyde sulfoxalate (as sold by E. I. du Pont de Nemours & Co. under the trade name "Sulfoxite C"), to name but two.

The proportion of starch to be used in preparing the sizing bath requires no discussion here, since one employs enough so that the resulting dispersion, after cooking in water, has the desired viscosity and solids content required for the sizing operation. The particular type of starch used will determine the amount that must be used to achieve a given viscosity. As mentioned, the use of starch dispersions for warp sizing is standard practice for other types of fibers, and the basic sizing procedures, dispersion viscosities and solids, etc., will be well known to those familiar with the art.

According to one embodiment of our process, the polyacrylic yarn may be passed through a bath comprising an aqueous dispersion of starch containing the metallic salt or the metallic salt and a reducing agent. As stated, the starch should preferably be a derivative containing free acidic groups, or the salts of such groups. Specific applications of this method will be found in the subsequent examples.

In a variation of this method, the yarn may first be passed through an aqueous solution (preferably heated) of the metallic salt, or the metallic salt and a reducing agent. The yarn treated in this manner may then be dried, if desired. Subsequently, the yarn, whether dried or coming directly from the metallic salt bath, is passed through the starch dispersion in the manner ordinarily employed for sizing yarns. This method is sometimes preferred, particularly where the original manufacturer of the polyacrylic yarn treats it with the metallic salt, and then sells the yarn to a processor who may then size it, prior to weaving, by means of an ordinary starch sizing operation. Here too, however, the starch should preferably be of the type heretofore described.

In a further variation of our process, the metallic salt may be added directly to the spinning dope, prior to formation of the fibers (employing, of course, an organic solvent soluble metal salt or complex). Thus, the yarn subsequently resulting from this dope will already contain the metallic salt and will be receptive to subsequent sizing with starch (particularly starch of the type herein described).

In general, we have found that elevated temperatures at the time of impregnating yarn with the metallic salt

increases the efficiency of our process. This is especially noted in those cases where the yarn is first passed through a bath comprising an aqueous solution of the salt, and is subsequently sized with the starch.

Regardless of whether the yarn is first passed through an aqueous solution of the metallic salt, or whether it is sized directly in an aqueous dispersion of starch containing the metallic salt dissolved therein, we have found that the salt may be present in the water in a wide range of concentrations. Thus, yarns have been treated successfully according to our process with as little as 0.2 part of the metallic salt per 100 parts of water in the yarn bath, and on the other hand the salt may be present in the bath up to the limit of its solubility in water. Thus, it will be apparent from the subsequent examples that we have employed metallic salts in aqueous solutions of the order of 15% concentration, and undoubtedly higher proportions would be feasible, depending of course on the solubility of the particular salt.

In testing yarn sized according to our process, we ordinarily use an instrument known as a Duplan cohesion tester. This instrument measures the number of strokes required to break a given yarn. Whereas a polyacrylic yarn sized with ordinary starch and tested in this manner ordinarily breaks after 20-40 strokes, it will be noted from the following examples that yarn sized according to our process requires in all cases at least 100 strokes and sometimes well over 400 strokes before breaking.

The following examples will further illustrate the embodiment of our invention:

Example I

A starch derivative was first prepared, according to the method of copending application, Serial No. 756,106, by suspending 100 pounds of corn starch which had been acid converted to a degree known in the trade as 60 acidity, in 125 pounds of water. The pH was adjusted to 7.0 with an aqueous solution of 2.5% NaOH. Then 3 pounds of maleic anhydride was slowly added in 1/4 pound portions during which the pH of the milk was kept constant at 7.0 by additions of dilute NaOH (2.5% solution in water). After agitating for 2 hours after the final addition of maleic anhydride, the starch was filtered, washed, and resuspended in 125 pounds of water, and 15 pounds of sodium bisulfite were added, with constant agitation. After 16 hours, the starch product, which was now a mono-ester containing both carboxylic and sulfonic acid groups, was filtered, washed and dried.

Fifteen pounds of the above starch derivative were suspended in a solution of 1 pound copper sulfate in 100 pounds water. A half pound of hydroxylamine sulfate was then added, and the suspension was cooked at 205° F. for 20 minutes and held at 200° F. throughout the subsequent sizing operation. Yarn from one and one-half inch staple polyacrylic fiber, known as "Acrilan" was sized with this dispersion in the usual manner.

The sized yarn was tested with the Duplan cohesion tester. Yarn sized with the above mixture broke only after 407 strokes, whereas the same type of yarn, treated only with a suspension of the above-described starch derivative, without the metallic salt, broke after 30-40 strokes.

Example II

Example I was repeated except that the starch used was a corn starch which had been oxidized with sodium hypochlorite to a degree known in the trade as 87 fluidity (there was no subsequent treatment with maleic anhydride and bisulfite). As a result of this oxidation the starch contained free carboxylic groups or the sodium salt of such groups. Acrilan yarn treated in the manner of Example I, but using the above mentioned starch base, broke after an average of 101 strokes when tested in the Duplan cohesion tester. In contrast, yarn sized merely

with the above mentioned starch, without the use of the copper sulfate, broke after only 31 strokes.

Example III

Ten pounds of a lightly converted corn British gum of about 10-15 fluidity (of the type sold by National Starch Products Inc. under the trade name "Spungel") were cooked in 100 pounds of water in which 0.5 pound of copper sulfate and 0.25 pound Sulfoxite C had been dissolved. After cooking 20 minutes at 205° F. the dispersion was pumped to a size box where the temperature was maintained at 200° F. throughout the subsequent sizing operation. Acrilan yarn was sized with this dispersion in the usual manner. When tested in the Duplan cohesion tester, yarn sized in this fashion broke after an average of 105 strokes while the same type of yarn sized with the British gum dispersion, in the absence of copper sulfate and Sulfoxite C, broke after only about 38 strokes.

Example IV

Example I was repeated using the starch derivative described therein; however, instead of employing copper sulfate and hydroxylamine sulfate, 15 pounds of the starch derivative were dispersed in 100 pounds of water containing dissolved therein 0.5 pound of stannous chloride. Acrilan yarn sized with this dispersion and tested in the Duplan cohesion tester, broke after an average of 228 strokes as compared to only 30-40 strokes for the same type of yarn sized only with the starch derivative in the absence of the stannous chloride.

Example V

Example IV was repeated except that in place of the 0.5 lb. of stannous chloride, we used 1.0 lb. stannic chloride. Acrilan yarn sized with this material broke after an average of 407 strokes on the Duplan cohesion tester.

Example VI

Example IV was repeated except that in place of the 0.5 lb. stannous chloride, we used 1.0 lb. chromic chloride. Acrilan yarn sized with this material, in the manner heretofore described, broke after an average of 457 strokes.

Example VII

Acrilan yarn was passed through a solution containing 1% by weight of ceric sulfate, maintained at 205° F. After passing through the solution, the yarn was candried. The impregnated yarn was then passed through a dispersion of the starch derivative described in Example I, the dispersion comprising 15 lbs. of the starch derivative in 100 lbs. of water. The sized yarn was then dried, and when tested in the Duplan cohesion tester, it withstood 356 strokes before breaking.

Example VIII

Example IV was repeated except that in place of 0.5 lb. stannous chloride, we used 1.0 lb. of bismuth nitrate. Acrilan yarn sized with this material broke after an average of 243 strokes when tested on the Duplan cohesion tester.

Example IX

Example I was repeated except that the concentration of copper sulfate was reduced from 1 lb. to 0.2 lb. and in place of 0.5 lb. hydroxylamine sulfate, we used 0.1 lb. Sulfoxite C. Acrilan yarn sized with the material of this example and tested as heretofore described broke after an average of 308 strokes.

Similar results were obtained when the concentration of copper sulfate was increased from 1 lb. to 15 lbs. and that of the hydroxylamine sulfate was increased from 0.5 lb. to 7.5 lbs.

Example X

Example VII was repeated except that in place of the ceric sulfate solution we used a solution containing 1%

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copper sulfate and 0.5% hydroxylamine sulfate by weight. Acrilan yarn impregnated with this solution and then sized as in Example VII withstood 350 strokes before breaking when tested as heretofore described.

Example XI

Example I was repeated except that in place of the starch derivative described therein, we used 10 lbs. of untreated corn starch. In another repetition of this example, we used 10 lbs. of untreated sago starch to replace the starch derivative of Example I. While yarn treated according to Example I, using these raw starches, indicated a substantial improvement as compared to treatment with these same starches in the absence of the copper sulfate, the improvement was less marked as compared to that obtained when using the starch derivative containing acidic groups (or their salts).

Example XII

Example I was repeated except that instead of sizing Acrilan, we sized spun Orlon yarn. The thus sized yarn was remarkably improved, particularly in that it showed very little tendency for the fibers to splay outward on breaking, as compared with spun Orlon sized similarly but without the use of the copper sulfate.

Example XIII

Example I was repeated except that copper acetate was used in place of the copper sulfate. Acrilan yarn sized with this material withstood 211 strokes before breaking when tested on the Duplan cohesion tester.

Summarizing, our process makes possible the effective use of starch as a size for yarns made from polyacrylic fibers. This is accomplished by sizing the yarns with starch (preferably a starch derivative containing free acidic groups or the salts of such groups) in the presence of a metallic salt of the type heretofore described. Depending upon the particular circumstances, innumerable variations may be made in working procedures and ingredients, within the spirit and scope of our invention.

We claim:

1. The process for warp sizing polyacrylic yarns to condition the same for weaving which comprises subjecting the yarn to the conjoint action of a starch size and a metallic salt solution in which the metallic salt is selected from the group consisting of stannic, stannous, ceric, chromic, chromous, bismuth and cuprous salts.

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2. The process for warp sizing polyacrylic yarns to condition the same for weaving which comprises impregnating the yarn with a size containing an aqueous dispersion of starch and a solution of a metallic salt selected from the group consisting of stannic, stannous, ceric, chromic, chromous, bismuth and cuprous salts.

3. The process of claim 2 in which the impregnation is carried out at an elevated temperature.

4. The process for warp sizing polyacrylic yarns to condition the same for weaving which comprises impregnating the yarn with a metallic salt selected from the group consisting of stannic, stannous, ceric, chromic, chromous, bismuth and cuprous salts and then sizing the thus impregnated yarn in an aqueous starch dispersion.

5. The process of claim 4 in which the step of impregnating the yarn with the metallic salt is carried out at an elevated temperature.

6. The process for warp sizing polyacrylic yarns of claim 1 in which the starch is a starch derivative containing free acidic groups.

7. The process for warp sizing polyacrylic yarns of claim 1 in which the starch is a salt of a starch derivative containing free acidic groups.

8. The process of claim 4 in which the starch is a starch derivative containing free acidic groups.

9. The process of claim 4 in which the starch is a salt of a starch derivative containing free acidic groups.

10. The process for warp sizing polyacrylic yarns to condition the same for weaving which comprises subjecting the yarn to the conjoint action of a starch size and a solution of a cupric salt in conjunction with a reducing agent to reduce the cupric to a cuprous salt.

11. The process for warp sizing polyacrylic yarns to condition the same for weaving which comprises impregnating the yarn with a size containing an aqueous dispersion of starch and a solution of a cupric salt in conjunction with a reducing agent to reduce the cupric to a cuprous salt.

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