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3,061,470 SIZING TEXTILE YARNS

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The present invention relates to the sizing of textile yarns, such as those composed wholly or partly of Dacron, with tough, flexible, water-soluble polymers which are the reaction products of polyalkylene ether glycols and aryl diisocyanates.

Heretofore, starch has been used almost exclusively as the basic ingredient of textile yarn sizing formulas. Some advances have been made in the use of synthetic size materials other than modified starch, especially in connection with synthetic yarns. However, these advances have been painfully slow despite the urgent need to conquer the stream pollution problem created by starch being dumped into streams from desizing units. Earlier synthetic sizing materials have met with very limited success because of their high cost and because they are only useful with a limited number of fibers. Dacron has been a particularly difficult fiber to size with any prior art materials and spun Dacron yarn sizing has remained a major textile problem prior to this invention.

It is an object of this invention to provide a composition and process by which textile yarns in general and spun Dacron yarn in particular may be readily sized on conventional equipment to provide excellent weaving efficiency and minimum shedding. Another object of the invention is the provision of a synthetic size which may be easily desized with plain water and dumped into streams without seriously polluting them.

It is one object of this invention to make high molecular weight, water-soluble, tough, flexible, film-forming polymers of polyalkylene ether glycols and aryl diisocyanates. Another object of the invention is the provision of control steps in the polymerization of polyalkylene ether glycols with aryl diisocyanates to control the properties of the polymers thus formed.

Another object of the invention is the provision of an inexpensive method of advantageously sizing and desizing textile yarns while substantially eliminating stream pollution problems. These and other objects of the invention will be more readily apparent from the following detailed description.

The novel polymers of this invention are particularly characterized by their water-solubility and their film-forming properties. They are readily water soluble, making them easy to apply to textile yarns as a size, and they retain their solubility so that desizing may be accomplished by a simple water wash. The films formed from water solutions of these new polymers are very tough and flexible and strong, especially as contrasted with the brittle films of the polyethylene ether glycol polymers alone and the prior art materials produced with water-insoluble reaction products of polyalkylene ether glycols and aryl diisocyanates, which materials are sometimes rubbery and sometimes crumbly.

These water-soluble reaction products of polyalkylene ether glycols and aryl diisocyanates have outstanding advantages over prior art sizing materials in weaving efficiency and in terms of running efficiency on conventional slashers. Good yarn penetration even in the absence of a separate wetting agent is obtained at temperatures of about 120-180° F. Hard size at the squeeze roll is substantially eliminated. There is no sticking on conventional drying cans. Separation of yarns at the split rods is smooth and even, and broken ends seldom, if ever, appear. At the same time, the size holds the fibers of in-

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dividual yarns in a very close, tight, unitary relationship for efficient weaving. These last two seemingly contradictory advantages are amply evidenced by the fact that spun Dacron yarns, for example, are so adhesively bound by the size of this invention that their diameter is actually substantially reduced by the sizing operation while the same yarns separate at a greater distance ahead of the split rods than the same yarns sized with conventional materials.

POLYMER PREPARATION

In making the polymers according to this invention one molar equivalent of a substantially anhydrous polymer of polyalkylene ether glycol having a molecular weight of from about 750 to 20,000 is catalytically reacted with from about 1 to 2 molar equivalents of an aryl diisocyanate (in practice slightly more than 1 mol is required and less than 2 mols is needed to avoid the danger of rapidly forming water-insoluble polymers) to produce polymers of extremely high molecular weight and the reaction is abruptly halted at a point just short of water insolubility. Preferably the molar ratio is from about 1¼:1 to 1½:1 of diisocyanate to glycol, respectively. The molar ratio is extremely important as too much diisocyanate rapidly produces water-insoluble products and too little diisocyanate produces brittle polymers which make weak films which are unsuitable for sizing purposes.

The abrupt halting of the reaction may be accomplished by the addition of a stopping agent which reacts with isocyanate radicals to block further reaction with the glycol. Such stopping agents include water, all monohydroxy alcohols including both saturated and unsaturated long chain alcohols, organic monoamino compounds, aryl monohydroxy compounds and the like. However, it has been found that in terms of weaving efficiency, water-stopped polymers are preferable to those stopped with amines and aryl hydroxy compounds. Aliphatic monohydroxy alcohols are still further preferred, as polymers so stopped have been found to maintain even better weaving efficiency over a period of time when used as a size. Methanol, being both inexpensive and efficient, is an excellent stopping agent for abruptly halting the polymerization reaction at the right point. The minimum amount of stopping agent to be added will vary according to the excess of diisocyanate used. While a theoretical minimum may be readily calculated, it is preferred to add at least a molar equivalent for the isocyanate used, as a safe excess. Additional quantities are ordinarily not harmful.

The reaction should proceed as far as reasonably possible short of the point of water-insolubility to obtain polymers having the most desirable film strength. For example, if the reaction is carried out under standardized conditions and water insolubility is first found to occur after a certain time X, products made in accordance with this invention may be made by duplicating the conditions except that reaction is halted at a time less than time X and greater than 80% of X.

Many methods may be used to determine the end point at which the reaction should be stopped to obtain a polymer that will provide tough flexible films which are readily water-soluble. In commercial production where everything is standardized, an empirical time-temperature relationship may be established by trial and error. After a little experience with given materials, a skilled chemist can tell the end point by visual inspection of the reaction mass—i.e. its viscosity, reaction to stirring, stringiness, etc. Also with any given reactants, empirical viscosity determinations may be used.

The polymerization time and temperature may be varied over a considerable range so long as the reaction is stopped at the critical point. The reaction must be carried out at a temperature above the melting point of

the polyalkylene ether glycol. However, the reaction proceeds slowly unless the temperature is elevated above about 70° C. but the temperature should not exceed 200° C. because higher temperatures tend to decompose the polyoxyalkylene chains. The preferred range is from about 100° C. to 150° C. The time of the reaction is a function of the temperature, the reactants, the catalyst and other factors. Suitable times have varied from 8 minutes to about an hour.

The term "polyalkylene ether glycols" as used throughout the specification and claims refers to polyethers which are derived from alkylene oxides or glycols or from other heterocyclic ethers such as dioxolane, and which may be represented by the formula $\text{HO}(\text{RO})_n\text{H}$, in which R stands for a lower alkylene radical and n is an integer greater than 1. Not all the alkylene radicals present need be the same and polyethers containing a mixture of radicals can be used, although the choice of radicals should be such that the resulting polyether is water soluble. These polyalkylene ether glycols are either viscous liquids or waxy solids. The molecular weights of the polyalkylene ether glycols which are most useful in the process of this invention are at least 750 and may be as high as 20,000. The preferred glycols are the polyethylene ether glycols.

A wide variety of aryl diisocyanates may be used in this invention, but monophenyl diisocyanates are preferred. Suitable compounds include 2,4 toluene diisocyanate, *m*-phenylene diisocyanate, 4-chloro-1,3 phenylene diisocyanate, methylene-bis-(4 phenyl isocyanate), naphthalene-1,5-diisocyanate and the like.

Any catalyst known to be useful in the reaction of polyalkylene ether glycols with aryl diisocyanates may be used in the present invention including the tertiary organic bases of U.S. Patent No. 2,692,874 such as triethylamine, pyridine, tri-*n*-butylphosphine, their acid salts and the like.

However, it has been found that particularly good results are obtained by using organo-metal salts, such as cobalt naphthenate and similar salts of lead, zinc, copper and manganese. The organic radicals may be either aliphatic or aromatic residues.

The term "substantially anhydrous polymer" is used to define a polymer containing less than about 0.5% moisture. It has been found that some commercial polyalkylene ether glycols containing as much as 0.5% moisture react improperly to provide films of poor strength, making them unsuitable for textile sizes. In practice, the moisture content of the polyalkylene ether glycols will be kept as low as possible.

SIZING PROCEDURE

Sizing yarns in accordance with this invention is a matter of utmost simplicity. The novel polymers may be dissolved in water and used at any temperature between room temperature and the boil. However, excellent yarn penetration is obtained at temperatures between 120° F. and 180° F. and higher temperatures are entirely unnecessary. Conventional equipment is completely satisfactory.

A one-piece size is satisfactory but the invention is not limited thereto; suitable additives may be used if desired, for example, a small quantity of a silicone has been found to impart excellent qualities of lubricity thereby improving weaving efficiency. The amount of silicone used will be from about 0.01% to 1% and preferably about 0.25%. Somewhat larger quantities may be used in some instances but such uses are merely wasteful. Furthermore, it has been found that raising the addition of ammonia to raise the pH of the solution to about pH 8.5-9.5 also provides a definite improvement in weave room performance, apparently by reduction of any tendency of the polymers to pick up moisture. The amount of size to be applied will vary somewhat according to the nature of the fibrous materials, the type of

yarn, the denier or count and the like but in general 2.5% to 5% polymer solids on the weight of the yarn provides a suitable size. The concentration of the sizing solution may vary over a fairly wide range of from about 2% to 15% but a 4% to 8% solution of the polymer is preferred.

In sizing operations, hygroscopic properties of the polymer must be minimized because weaving is normally done under very high humidity conditions. The use of polyurethanes end blocked with alkoxy groups, i.e. alcohol stopped reaction products of the invention, has been found to be particularly valuable in terms of lowered hygroscopic tendencies. Silicones are very effective in reducing any stickiness which may tend to occur as a result of moisture pick-up of hygroscopic polymers.

Surprisingly, the silicone rises through the polymers of aryl diisocyanate and polyalkylene ether glycol when mixtures of the two are cast into films from an aqueous medium. This provides a sort of two layer effect permitting the hydrophobic properties of the silicone to be effectively utilized.

Thus, in the preferred manner of sizing, one will use an aqueous medium containing an alcohol stopped water-soluble polymer of the invention and a silicone with the medium having a controlled pH of from about 8.5-9.5. Yarns sized in accordance with this preferred procedure have a coating of polymer topped by a coating of silicone.

The stability of the polymer in solution is excellent so that it may be stored in any of its liquid or solid forms and its good water solubility permits mixing at any point in the mill whereby a separate mixing operation and operator, as required for starch sizing, may be eliminated.

The invention is described both in the specification and claims in terms of sizing textile yarns and it will be understood that the term "yarn" includes both spun fiber yarns and filament yarns. The invention is particularly applicable to spun Dacron ethylene glycol terephthalic acid polyester, spun mixtures of cotton and Dacron, cotton, viscose and acetate and the like.

In some instances a permanent size is desirable to provide a loom finished fabric. In such instances, the polymers of this invention may be further reacted in situ on yarn to provide the desired products. In these reactions, formaldehyde, acetaldehyde, acrolein, other aldehydes, and/or aldehyde donors such as methylol melamines, methylol ureas, methylol ethylene ureas, copolymers of acetone and formaldehydes, methylol acetylene diureas and the like may be added to the sizing solution preferably in the presence of an acidic catalyst so that they will react with the polymer on the slasher dry cans to produce water-insoluble cross-linked films on the yarn.

The invention will be better understood by reference to the following typical examples:

Example 1

92 pounds of substantially anhydrous polyethylene ether glycol in a molecular weight range of 6000-7500 (Carbowax 6000) was melted in a 50 gallon reactor equipped with a reflux condenser and a stirrer. When the temperature reached 70° C., 4 pounds and 3 ounces of 2,4 toluene diisocyanate (Nacconate 100) was added with stirring. 183 grams of a 6% solution of cobalt naphthenate was added forthwith to catalyze the reaction. At the end of the addition, the temperature had risen to 88° C. as heating was continued throughout the reaction. In about 20 minutes the reaction temperature reached 140° C. This temperature was maintained for 15 minutes while stirring continued. At the end of the 15 minute period, 9 pounds of isopropanol were added and stirred into the mixture to halt the reaction and heating was stopped. Water was then added in a quantity sufficient to make a 25% solution of the polymer which was then ready for further dilution and use as a size. After addition of the diisocyanate and catalyst, the

reacting mass became more viscous as the reaction proceeded. Towards the end of the reaction period, the reaction mass was stiffening and would string out several inches behind a stirring rod. There was little change in physical appearance on addition of the methanol except for the relatively stiff mass to take on a swollen, slightly rubbery or jelling appearance. On addition of the water, the entire mass dissolved rapidly to produce a clear, neutral, slightly yellow, transparent somewhat viscous solution.

Example 2

To 35 grams of molten (120° C.) polyethylene ether glycol of a molecular weight range of 6000-7500, there was added 1 gram of 2,4-toluene diisocyanate and 5 drops of cobalt naphthenate solution (6%). The temperature was maintained for 5 minutes after which water was added in a quantity sufficient to make a 10% solution. The reaction proceeded as in Example 1, except that the smaller quantity required less time for reaction to the same point and reaction was stopped with water rather than methanol. The appearance of the two solution products was not distinguishable to the naked eye. The product of this example had a viscosity of 333 centipoises.

Repeating this example using m-phenylene diisocyanate or methylene-bis-(4-phenyl isocyanate) (in 50% benzene solution) instead of 2,4-toluene diisocyanate produced products of similar appearance and utility as a size.

Example 3

A warp of several thousand ends of 100% spun Dacron yarns was sized on conventional synthetic slasher equipment having a heated size-box, standard squeeze rolls and Teflon-coated dry cans. The yarns were impregnated by passing them through the size box containing a water solution of the product of Example 1 diluted to 6% solids and brought to pH 9 with ammonia. The size box temperature was kept at 150° F. and the squeeze rolls were set to leave 3.5% solids on the yarn. Drying was completely conventional with dry can temperatures of about 200° F. The slasher operated smoothly without hard size problem, with no sticking on the cans and excellent action was noted at the split rods. It appears as though splitting might be a smooth tear for no jagged edges were noted at the split lines and the split ran back from the rods a greater distance than normal.

A beam of the sized yarns was placed on a loom and readily woven into an all Dacron fabric of standard plain weave construction. Good weaving efficiency was noted immediately and shedding was minimized.

Complete desizing was effected by washing the woven fabric for 30 minutes in lukewarm water, even without a surface active agent.

Example 4

In a suitable reaction vessel there is placed 50 parts by weight of dimethyl silicone oil (5000 centipoises), 20 parts by weight of perchlorethylene, 25 parts toluene, and 5 parts oleic acid. The resulting mixture agitated until solution was complete.

A size mixture was prepared as in Example 3 except there was dispersed in the aqueous mixture 2% by weight of the above silicone solution. The size mixture was then applied according to the procedure of Example 3 to a warp of several thousand ends of 100% spun polyethylene terephthalate (Dacron) yarns. The sized yarns appeared to have more lubricity than those from the preceding example, and this may account for the even greater weaving efficiency noted.

This example was repeated using methyl hydrogen silicone, chain stopped with trimethyl silicone, in place of the dimethyl silicone oil and the results were substantially duplicated. Other silicones useful in the treatment of textiles may be substituted for those listed above or the

coated yarns may be top coated with chlorosilane vapors if desired.

Example 5

To prepare a loom finished fabric, an all cotton warp was sized with a 5% solution of a product prepared in accordance with Example 3 to deposit 5% solids (weight basis) thereon. At the time of mixing the sizing solution (just prior to use), 0.1% of formaldehyde was added. A conventional cotton slasher was used with the size box heated to a temperature of 130° F. Excellent running conditions were noted as in Example 3. The sized warp was woven into an all cotton fabric. Weaving efficiency was good and shedding was minimized.

Because of the formaldehyde, the size film had become insoluble and could not be washed out, thus providing a high-quality loom finished cotton fabric.

Those skilled in the art will find that certain changes may be made in the precise conditions, proportions and procedures set forth above without departing from the invention as defined in the claims.

I claim:

1. The method of sizing textile yarns which comprises sizing said yarns with a tough flexible polymer which is a water-soluble reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight prior to reaction in the range of from about 750 to 20,000.

2. The method of sizing textile yarns which comprises sizing said yarns with a tough flexible polymer which is a water-soluble reaction product of an aryl diisocyanate and a polyethylene ether glycol having a molecular weight range of from about 750 to 20,000.

3. The method of sizing a textile yarn comprising sizing said yarn with from about 2.5% to 5% of its weight of a tough flexible polymer which is a water-soluble reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight in the range of from about 750 to 20,000 and a lesser amount of a silicone by impregnating said yarn with an aqueous medium containing said silicone and said polymer and thereafter heating the thus impregnated yarn to dry it.

4. The method of sizing ethylene glycol terephthalic acid polyester yarn which comprises sizing said yarn with a tough, flexible, water-soluble polymer which is a reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight range of from about 750 to 20,000.

5. The method of sizing as set forth in claim 4 wherein the sizing composition contains, in addition, a small quantity of a dispersed silicone.

6. The method of sizing yarn which comprises sizing said yarn with a tough, flexible, water-soluble polymer which is a reaction product of an aryl diisocyanate and a polyethylene ether glycol having a molecular weight range of from about 6,000 to 7,500.

7. The method as set forth in claim 6 wherein said polymer on said yarn comprises from about 2.5% to 5% of the weight of said yarn.

8. The method as set forth in claim 7 wherein said yarn is comprised at least in part of ethylene glycol terephthalic acid polyester.

9. The method as set forth in claim 7 wherein the sizing composition also contains a small quantity of a silicone.

10. The method of sizing spun ethylene glycol terephthalic acid polyester yarn which comprises impregnating said yarn at about 140° F. with an aqueous solution containing about 6% of a water-soluble, tough, flexible, film-forming polymer which is a reaction product of 2,4-toluene diisocyanate and a polyethylene ether glycol having a molecular weight range of from about 6000 to 7500 and thereafter drying the thus impregnated yarn, the amount of pick-up of said solution being regulated to provide a deposit of from about 2.5% to 5% of polymer based on the weight of the yarn.

11. The process of producing a permanently sized textile yarn comprising sizing said yarn with a tough, flexible, water-soluble polymer which is a reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight of from about 750 to 20,000 and reacting said polymer with a water-insolubilizing agent on said yarn.

12. The method of sizing yarns which comprises sizing said yarns with an alcohol stopped, water-soluble, tough, flexible polymer which is the reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight of from about 750 to 20,000.

13. A textile product comprising a yarn sized with a tough flexible polymer which is a water-soluble reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight range of from about 750 to 20,000.

14. A new textile product comprising an ethylene glycol terephthalic acid polyester yarn sized with a tough, flexible, water-soluble polymer which is a reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight of from about 750 to 20,000.

15. A yarn sized with a tough, flexible, water-soluble polymer which is a reaction product of a monophenyl diisocyanate and a polyethylene ether glycol having a molecular weight range of from about 750 to 20,000.

16. A yarn as set forth in claim 15 wherein the yarn

is comprised at least in part of ethylene glycol terephthalic acid polyester and the amount of said polymer on said fiber is from about 2.5% to 5%, calculated on the weight of said polyester.

17. A loom finished fabric comprised of woven warp and filling yarns wherein the warp yarns are coated with a tough, flexible, water-insoluble polymer formed by the reaction of an aryl diisocyanate with polyalkylene ether glycol having a molecular weight of from about 750 to 20,000.

18. A textile yarn sized with a tough, flexible polyurethane which is the reaction product of an aryl diisocyanate and a polyalkylene ether glycol having a molecular weight of from about 750 to 20,000, said polyurethane being water-soluble and having its molecules end-blocked with alkoxy groups to preserve its water solubility.

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