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WATER-SOLUBLE MULTIFILAMENT YARN
AND PROCESS FOR MAKING IT

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This invention relates to the production of filaments, fibers and multifilament threads and yarns of a water-soluble hydroxyethyl cellulose ether; and more especially it concerns the production of such textile articles having tenacities of at least 0.7 gram per denier, and ultimate elongations ranging from around 10% to 30%.

These water-soluble filaments, and staple fibers and threads made therefrom, have utility for many purposes, as in the manufacture of certain types of lace wherein the soluble threads or yarns of this invention are interwoven with permanent fibers or threads and are later dissolved out of the fabric by a solvent such as water which does not dissolve the permanent fibers, thereby preserving the desired pattern formed by the latter. In another application these soluble threads are twisted with permanent water-insoluble threads in such manner that the permanent component of the twisted composite yarn has zero twist. A textile article then is woven from the composite yarn, and the soluble thread is dissolved out with water or other suitable solvent which does not dissolve the permanent threads, thereby leaving a fabric made of threads of untwisted filaments. The water-soluble threads and filaments of the invention also may be used as carriers of very fine worsted thread in the manufacture of "100% gossamer fine-worsted" textiles.

Heretofore, threads of silk, cotton, wool and various synthetic resins such as vinyl chloride-acetate resins have been used in the manufacture of soluble fibers or threads for these and other special applications. The tendency always has been toward the use of fibers and threads that can be dissolved by the simplest possible solvent system. In recent years, fibers made from certain salts of alginic acid which are soluble in mild soap solutions and in water have been introduced and have tended to dominate this field. However, not only are such products rather costly but, moreover, the alginic acids available vary rather unpredictably both in quantity and in their physical properties.

Although water-soluble hydroxyethyl celluloses have been commercially available for several years, previous attempts to prepare useful water-soluble multifilament yarns from these resins have been unsuccessful. This apparently has been due in large measure to the fact that those hydroxyethyl cellulose resins initially available and useful as film-forming materials, sizing agents, binders and the like have had molecular weights insufficiently high to provide multifila-

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ment yarns possessing physical properties adapting them for textile services.

According to the present invention, highly water-soluble continuous stretched filaments, fibers, and multifilament yarns and threads of hydroxyethyl cellulose ethers are produced which have dry tenacities of over 0.7 gram per denier, ranging upward to 1.25 or more grams per denier, and which have ultimate elongations ranging from 10% to 30% or more. This is accomplished by wet-spinning an aqueous solution of a water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, and preferably of over 2,000 centipoises—e. g., 4,000 or more—as measured with a Hoepffler viscosimeter. The yarns made from the aforesaid preferred cellulose ethers commonly have dry tenacities of over one gram per denier. Preferably the water-soluble hydroxyethyl cellulose used has been treated by dialysis or in other suitable manner so as to be substantially free from inorganic compounds.

The relatively high viscosity water-soluble hydroxyethyl celluloses used in the production of filaments and yarns in accordance with this invention may be made in well-known manner. Thus, according to one process, an alkali cellulose is made by immersing sulfite wood pulp in an 18% caustic soda solution, squeezing out surplus caustic solution, shredding the resultant mass at temperatures of 15° C.—45° C. for two to three hours. Thereafter, without substantial further aging of the shredded alkali cellulose, it is reacted with ethylene oxide in the general manner described in Example IV of the A. V. Schorger Patent No. 1,914,172. Under such conditions, hydroxyethyl cellulose are produced, 5% aqueous solutions of which have specific viscosities at 20° C. of 1,000 centipoises or more; and commonly even 2% aqueous solutions thereof have specific viscosities at 20° C. of around 300 to 3,600 or more centipoises. Such products are very suitable for use in the production of the water-soluble yarns of the invention. The inorganic compounds can be removed from the hydroxyethyl cellulose by dialysis, as indicated in the aforesaid Schorger patent.

In the practice of one preferred form of the invention, such an hydroxyethyl cellulose, substantially free from inorganic salts and hydroxides, is dissolved in water to form a spinning solution containing between about 3% and 30% of the cellulose ether, and usually containing between 5% and 20% thereof, the amount of the cellulose ether in the spinning solution varying

inversely with the molecular weight of the ether, as measured by its viscosity. The temperature of the aqueous spinning solution influences its consistency, and can be varied to allow greater latitude in solution concentration. Temperatures around atmospheric have given good results, but higher temperatures up to 100° C.—e. g., 50° C.—facilitate the use of higher concentrations of the cellulose ether or the use of cellulose ethers of higher molecular weight. Particularly when using those hydroxyethyl celluloses, 5% aqueous solutions of which have viscosities at 20° C. of around 2,000 centipoises or more, it is preferred to extrude the spinning solution while maintained at elevated temperatures between 40° C. and 100° C. When acetone is used as the coagulant the temperature of the solution being spun preferably should not exceed the boiling point of acetone.

When preparing spinning solutions of resinous water-soluble hydroxyethyl celluloses (a 5% aqueous solution of which cellulose ether has a viscosity at 20° C. of 1,000 centipoises or more), more rapid dissolution of the solid cellulose ether in water and smoother spinning solutions free from gels are achieved by first wetting the said ether with acetone. The latter is miscible with water but is a non-solvent for such hydroxyethyl cellulose. Acetone in the viscous spinning solution facilitates the expelling of air bubbles from such solution when the acetone is present in small amounts around 5% to 15% by weight of the solution, especially when such solution is heated to temperatures around 50° C. to 100° C.

The spinning solution preferably is aged at room temperature or somewhat above for a time sufficient to free the solution from the air bubbles formed in the mixing operation. The aged solution then is forced under suitable pressure through a spinneret of standard type immersed within a coagulating liquid through which the coagulated filaments travel for a distance sufficient to give them a firm body and a strength sufficient to permit their being drawn from the coagulating bath to successive coagulant-removing and subsequent operations. Spinnerets having a plurality of orifices ranging from 0.003 inch to 0.01 inch in diameter have given excellent results. The rate of spinning is determined by the required period of exposure of the filaments to the coagulating bath to achieve a satisfactory degree of filament toughness; and periods of exposure of the spun filaments to the coagulating bath ranging from two to ten seconds conveniently can be used in conjunction with spinneret orifice velocities ranging from 50 feet to 200 feet or more per minute.

Among coagulating liquids found especially suitable for use with the high molecular weight hydroxyethyl cellulose ethers is acetone, which may contain up to about 20% of water. Acetone containing around 40%–50% of water causes severe swelling and weakening of the fibers. In place of acetone, other organic liquid coagulants effective in the process are the water-soluble mono- and polyglycols containing four or more carbon atoms in the molecule, such as butane-1,4-diol, hexane-1,3-diol and dimethoxytetraethylene glycol; and the class of water-soluble monoalkyl ethers of the glycols such as the monomethyl, monoethyl and monobutyl ethers of ethylene glycol and of diethylene glycol. Such glycols and glycolethers may contain up to about 10% of water. Concentrated aqueous solutions of various water-soluble inorganic salts also serve

effectively as coagulating liquids for the water-soluble hydroxyethyl celluloses. Among such salts may be mentioned the ammonium and alkali metal sulfates and sulfites, and the ammonium and alkali metal phosphates, such as dipotassium phosphate and diammonium phosphate. Usually more rapid coagulation occurs and tougher filaments are produced when the coagulating bath is maintained at elevated temperatures up to 100° C. or more than when it is held at room temperature; and temperatures around 70° C. to 95° C. are preferred. However, when acetone is used as the coagulant, the bath temperatures preferably are around 25° C.–35° C., and should not exceed the boiling point of acetone.

When a coagulating liquid other than acetone is employed, the coagulated filaments moving to the take-up bobbin are conducted first through a bath containing a liquid chosen primarily for its ability to remove the coagulating liquid clinging to the surface of the yarn, and then are conducted through one or more wash baths to complete the cleansing process. Organic coagulants such as the higher glycols and polyglycols and monoalkyl ethers of such glycols can be readily removed from the surface of the yarn by passing the yarn through a bath of acetone, isopropanol or other low boiling liquid which is not a solvent for the hydroxyethyl cellulose. When concentrated aqueous solutions of inorganic salts are employed as coagulant, however, rather more care must be used in selecting the washing liquid. It has been found that ethylene glycol and diethylene glycol monoethyl ether are particularly suitable for removing inorganic salt solutions from the surface of the yarn. Each of these liquids is miscible with concentrated aqueous solutions of ammonium and alkali metal sulfates and sulfites, and possesses the property of flocculating these inorganic salts to a form facilitating their removal by a simple washing operation with a non-solvent for the hydroxyethyl cellulose. When the coagulating salt is an ammonium or alkali metal phosphate, the salt in solution clinging to the yarn surface either flocculates when it comes into contact with the ethylene glycol or monoethyl ether of diethylene glycol or it goes into solution in these liquids. Such liquids also serve as superficial plasticizers for the water-soluble hydroxyethyl cellulose. When acetone is used as the coagulating medium and fibers produced may have greater resiliency, extensibility and toughness imparted thereto by including with the acetone a few per cent—e. g., 2% to 10%—of a water-soluble polyhydric alcohol or alcohol ether, such as ethylene glycol, diethylene glycol, propylene glycol, glycerine, or the monoethyl ether of ethylene glycol, or by passing the coagulated filaments or yarns through a bath of such a polyhydric alcohol or alcohol ether after emerging from the acetone bath.

The amount of plasticizer taken up by the filaments or yarns depends upon the contact time in the plasticizer bath and in the subsequent washing baths, and upon the temperature of the baths. Part or all of the plasticizer can be removed in these wash baths; but it is preferred that the filaments retain a plasticizer content of between 2% and 10% when an organic plasticizer is employed.

In the form of the invention wherein the filaments or yarns are passed from the coagulating bath into and thence through a flocculating

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and/or plasticizing bath, the filaments or yarns leaving the latter are drawn through one or more wash baths consisting of one or more volatile liquid non-solvents for the water-soluble hydroxyethyl cellulose but which are solvents for the plasticizer when the latter is used in the previous bath. The period of exposure of the filaments to the wash baths is sufficient to remove any last traces of the coagulant and any desired excess of the plasticizer. When two wash baths are employed, one or both may consist of acetone or isopropanol. The order of the isopropanol and acetone baths, when both are used, is immaterial. The wash baths usually are at around room temperature, but higher or lower temperatures may be used. The presence of as much as 25% of water in the wash baths is not objectionable.

Between the time that the spun filaments leave the spinneret orifices and the time the filaments leave the last treatment bath, they are subjected, either continuously or intermittently to tension sufficient to impart thereto a degree of stretch ranging up to 100% of the original length of the filaments leaving the spinneret. Higher degrees of stretch may be imparted to the yarn by passing the yarn, preferably while still containing enough moisture to provide a softening action, through a stretching tube maintained at an elevated temperature up to about 150° C. For most purposes an amount of stretch corresponding to around 40% to 60% of the original length of the filaments appears to be the optimum.

For effecting the stretching of the filaments, each of the treatment baths preferably is provided with an independently driven Godet unit. Successive godets operate at different speeds to provide the desired degree of stretch. The desired contact time of the yarn within each bath is secured by causing the yarn to make a suitable number of passes over these Godet units and through the bath. The stretched yarn leaving the last treatment bath is wound upon a take-up bobbin.

Following the wash baths, the spun stretched filaments or yarns on the bobbins are dried. This conveniently is done by heating for three hours or more in an oven at 50° C. They then are allowed to come to equilibrium with atmospheric temperature and humidity. When desired the stretched filaments may be collected, twisted and plied in any well known manner.

The following examples serve to illustrate the invention:

Example 1

A high viscosity water-soluble hydroxyethyl cellulose substantially free from inorganic compounds (a 5% aqueous solution of which had a viscosity at 20° C. of about 1,000 centipoises) was dissolved in water with agitation to form a 13% solution. After standing for twenty-four hours at room temperature to permit air bubbles to escape, the clear solution was pumped through a spinneret located beneath the surface of a coagulating liquid. A standard spinneret having ten orifices each 0.01 inch in diameter was used; and the pump was operated to provide a spinneret orifice velocity of 200 feet per minute. The coagulant used was a saturated aqueous solution of ammonium sulfate maintained at between 70° C. and 75° C. The filaments emerging from the coagulating bath were carried over pulleys into a second bath containing ethylene glycol at room temperature. The glycol served to flocculate and

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remove substantially all of the coagulant carried thereto from the coagulating bath. The glycol coated filaments then were carried over pulleys into and through two successive wash baths maintained at room temperature. The first bath consisted of isopropanol, and the second was acetone. Both baths were gradually diluted somewhat with the ethylene glycol; and the acetone bath also contained some isopropanol as the process continued. The filaments leaving the last wash bath were wound upon a take-up bobbin driven at a rate sufficient to impart a 50% stretch to the filaments during the spinning operation. Each of the baths, excepting the coagulating bath, had a driven Godet unit; and the filaments made several passes over these units to regulate the contact time of the filaments within the baths. The surface of the yarn at the take-up bobbin was clean and free from salt.

The final stretched filaments or yarns, after drying for twenty-four hours at 25° C. and 40% relative humidity, had a dry tenacity of 0.75 gram per denier and an ultimate elongation of 15%.

Example 2

A high viscosity water-soluble hydroxyethyl cellulose substantially free from inorganic salts and hydroxides (a 5% aqueous solution of which had a viscosity at 20° C. of about 2,200 centipoises), was dissolved in water to provide a 9% aqueous solution thereof. This solution was heated to 50° C. and was pumped through a spinneret having thirty orifices each 0.0045 inch in diameter, at a pressure providing an orifice velocity of 100 feet per minute. The spinneret was located beneath the surface of a liquid coagulant consisting of acetone containing not more than 10% of water. As the acetone became further diluted with water during the operation, it was replaced with fresh acetones. The filaments traveled about 60 inches in the acetone bath to facilitate the hardening thereof to the desired extent, and then were collected, drawn to and wound upon a take-up bobbin so driven as to stretch the filaments about 50% during the spinning operation. The final stretched filaments or yarns, after drying for about twenty-four hours at 25° C., had a dry tenacity of 1.25 grams per denier and an ultimate elongation of 22%. They were white in color, substantially free from inorganic salts and, despite the high molecular weight of the hydroxyethyl cellulose used, dissolved readily in water at room temperature.

By including in the acetone coagulating bath a few per cent—e. g., 2%–10%—of a water-soluble polyhydric alcohol or alcohol ether, such as ethylene glycol, glycerine, and the monomethyl and monoethyl ethers of ethylene and diethylene glycol, the resiliency, extensibility and toughness of the coagulated filaments and yarns can be improved.

Example 3

A high viscosity water-soluble hydroxyethyl cellulose (a 5% aqueous solution of which had a viscosity at 20° C. of about 1,000–1,050 centipoises) was dissolved in water to form a 13% aqueous solution, following the procedure described in Example 1. The solution was pumped under pressure through a spinneret of the type described in Example 2 at an orifice velocity of 100 feet per minute, the spinneret being located within a coagulating bath consisting of a saturated aqueous solution of dipotassium phosphate maintained at 70° C.–75° C. The filaments or yarns leaving the

coagulating bath were passed successively through (1) a bath of ethylene glycol; (2) an isopropanol wash bath; and (3) an acetone wash bath, and then were wound upon a take-up bobbin driven at a rate sufficient to stretch the filaments 50% of their original length. The ethylene glycol and wash baths were at room temperature. The resultant stretched filaments and yarns were white in color, clean, and their surfaces were substantially free from salt. After drying for twenty-four hours at 25° C., they had a dry tenacity of 0.8 gram per denier and an ultimate elongation of 30%.

It has been established that progressively stronger filaments and yarns possessing commercial utility are produced as the molecular weight of the water-soluble hydroxyethyl cellulose is increased above that corresponding to such a product the viscosity of a 5% aqueous solution of which is about 1,000 centipoises. Moreover, as the molecular weight of the cellulose ether increases above this minimum, the filaments and yarns spun therefrom by this invention can be given a higher degree of stretch during the stretch-spinning operation without injury thereto. On the other hand, it is noteworthy that multifilament yarns spun from the lower molecular weight hydroxyethyl celluloses such as one, a 5% aqueous solution of which possesses a viscosity at 20° C. of around 500 centipoises or less, generally are extremely weak and brittle and have little if any utility.

The invention is susceptible of modification within the scope of the appended claims.

We claim:

1. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said yarn having a tenacity of at least 0.7 gram per denier and an ultimate elongation of between 10% and 30%.

2. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said yarn having a tenacity of at least 0.7 gram per denier and an ultimate elongation of between 10% and 30%, and being substantially free from inorganic compounds.

3. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said yarn having a tenacity of at least 0.7 gram per denier and an ultimate elongation of between 10% and 30%, said yarn having therein a small amount of a water-soluble plasticizer for the hydroxyethyl cellulose.

4. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said yarn having a tenacity of at least 0.7 gram per denier and an ultimate elongation of between 10% and 30%, said yarn containing a small amount of a water-soluble glycol.

5. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said yarn having a tenacity of at least 0.7 gram per denier and an ultimate elongation of between 10% and 30%, said yarn containing a small amount of glycerol.

6. A stretched water-soluble multifilament textile yarn composed of a high molecular weight hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 2,000 centipoises, said yarn having a tenacity of at least 1.25 grams per denier and an ultimate elongation between 10% and 30%, and being substantially free from inorganic compounds.

7. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such spinning solution through a plurality of passages in a spinneret and into a liquid bath of a water-soluble coagulant for the hydroxyethyl cellulose, conducting the coagulated filaments thus produced through a bath of a water-soluble polyhydric alcohol while gathering the filaments to form a yarn, stretching the yarn at least 50% while passing through at least one of said baths, and then drying the yarn.

8. In a process for making a multifilament yarn from a high molecular weight water-soluble hydroxyethyl cellulose, the steps which comprise forming an aqueous spinning solution of such a hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such solution in the form of a plurality of filaments into a coagulating bath of acetone containing not more than 20% of water, gathering the coagulated filaments to form a yarn, stretching the yarn at least 50%, and then drying the yarn.

9. In a process for making a multifilament yarn from a high molecular weight water-soluble hydroxyethyl cellulose, the steps which comprise forming an aqueous spinning solution of such a hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 2,200 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, heating such solution to temperatures within the range between around 40° C. and 100° C., extruding the heated solution in the form of a plurality of filaments into a coagulating bath of acetone containing not more than 20% of water, gathering the coagulated filaments to form a yarn, and stretching the filaments at least 50% while passing through said bath and drying the yarn.

10. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such spinning solution through a plurality of passages in a spinneret and into a liquid bath of a concentrated aqueous solution of a water-soluble inorganic salt, thereby coagulating the hydroxyethyl cellulose, conducting the coagulated filaments thus produced through a bath of a water-soluble polyhydric alcohol which is a flocculant for said coagulant for a time at least sufficient to remove excess coagulant from said filaments while gathering the filaments to form a yarn, thereafter conducting the yarn through

a wash bath of at least one volatile liquid solvent for the said polyhydric alcohol which is a non-solvent for the hydroxyethyl cellulose, stretching the yarn at least 50% while passing through at least one of said baths, and then drying the yarn.

11. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such spinning solution through a plurality of passages in a spinneret and into a liquid bath of a water-soluble organic coagulant for the hydroxyethyl cellulose, conducting the coagulated filaments thus produced through a bath of a water-soluble polyhydric alcohol while gathering the filaments to form a yarn, stretching the yarn at least 50% while passing through at least one of said baths, and then drying the yarn.

12. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such spinning solution through a plurality of passages of a spinneret and into a bath comprising a concentrated aqueous solution of a water-soluble inorganic sulfate, conducting the resultant coagulated filaments thus produced through a bath of a water-soluble polyhydric alcohol for a time at least sufficient to remove excess coagulant from such filament, while gathering the filaments to form a yarn, thereafter conducting the yarn through a wash bath of at least one volatile liquid solvent for the said polyhydric alcohol which is a non-solvent for the hydroxyethyl cellulose and for said coagulant, stretching the yarn at least 50% while passing through at least one of said baths, and then drying the yarn.

13. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such solution through a plurality of passages of a spinneret and into a bath comprising

a concentrated aqueous solution of an alkali metal phosphate, conducting the coagulated filaments thus produced through a bath of a water-soluble polyhydric alcohol which is a solvent for said phosphate for a time sufficient to remove excess coagulant from said filaments, while gathering the filaments to form a yarn, thereafter conducting the yarn through a wash bath of at least one volatile liquid solvent for the said plasticizer which is a non-solvent for the hydroxyethyl cellulose and for said phosphate, stretching the yarn at least 50% while passing through at least one of said baths, and then drying the yarn.

14. Process for making a high molecular weight water-soluble multifilament yarn, which comprises forming an aqueous spinning solution of a high molecular weight water-soluble hydroxyethyl cellulose, a 5% aqueous solution of which has a viscosity at 20° C. of at least 1,000 centipoises, said spinning solution containing between 3% and 30% of said hydroxyethyl cellulose, extruding such spinning solution through a plurality of passages in a spinneret and into a liquid bath of acetone containing not more than 20% of water and a small amount of a water-soluble alcohol selected from the class consisting of the water-soluble polyhydric alcohols and the water-soluble monoalkyl ethers of ethylene glycol, while gathering the filaments to form a yarn, stretching the yarn at least 50% while passing it through such bath, and then drying the yarn.

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