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VISCOSE SPINNING SOLUTION FOR THE MANUFACTURE OF SHAPED ARTICLES FROM REGENERATED CELLULOSE

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The subject of the present invention is a process for the manufacture of fibres, threads or films from regenerated cellulose which are characterised by high strength and low swelling.

Owing to the fact that in recent times better qualities are required for these products so that they may be used for textile and technical applications, in this case mainly to make them suitable for use as tyre cord, attempts have been made to find ways and means of modifying the customary viscose process in order to obtain material having the desired properties.

Thus, methods are known in which so-called modifying agents are added to the viscose or to the spinning bath in order to retard the decomposition of xanthogenate and to reduce the gel swelling value, which also frequently improves the textile properties of the spun threads. At the same time, the other spinning conditions have also had to be adapted to these new conditions, and this may be achieved, for example, by the use of higher concentrations of zinc sulphate and lower concentrations of sulphuric acid in the precipitation baths or the use of a separate second bath in which the threads are subjected to a stretching process.

Compounds which produce these effects include a large number of mono- and polyamines and their alkoxylated products as well as polyglycol ethers of many different compositions and mixtures of the two classes of compounds.

The object of the present invention is to obtain threads which have a lower swelling value and at the same time a higher tensile strength and elongation by using certain additives in the customary viscose process. Another object of the invention is to provide special additives which may be used in the viscose process for improving the quality of the threads. Further objects of the invention will become evident in the following description and examples.

It has now been found that the above objects may be achieved particularly advantageously by the addition of those polyether sulphones to the viscose solution which are soluble in concentrations of at least 0.1% in 5% aqueous sodium hydroxide solutions and which preferably have a molecular weight between 300 and 20,000.

It is preferred to use those polyether sulphones in which for every four carbon atoms there is at least one ether oxygen atom or one sulphone group. Many different processes may be used for preparing the claimed ether sulphones, for example, linear or branched polyether thioethers, such as those described in French patent specification 1,201,171, may be oxidized with hydrogen peroxide, sodium hypochlorite, or similar oxidizing agents, or alternatively mono-, di- and polyvinyl sulphones, for example divinyl sulphone, dipropenylsulphone or p-di-vinylsulphonyl benzene may be added to monohydric or polyhydric alcohols, or alternatively the above-mentioned monohydric and polyhydric alcohols may be reacted with β-halogen-alkyl-sulphones, such as methyl-β-chloroethyl-sulphone, di-β-chloroethyl-sulphone and the like in the presence of hydrogen chloride binding agents.

The polyether sulphones have the particular advantage that they may be mixed homogeneously more easily with the viscose than the other additives previously mentioned, so that they are more effective. This has the result that the other spinning conditions, in particular the nature of the viscose and of the precipitating bath may vary within wider limits than is the case with many other modifying agents, so that a marked improvement in the quality of the fibres may be obtained even when spinning the usual commercial viscose in ordinary acid precipitating baths (i.e. baths having a higher concentration of sulphuric acid and of sodium sulphate and a lower concentration of zinc sulphate than indicated for the above-mentioned processes) followed by stretching in air after ordinary rinsing or centrifuging processes.

The compounds used in accordance with the invention may conveniently be employed by means of the dosing processes which are already known for example for adding dyestuffs to spinning solutions, because when the aqeous or alkaline solutions of these compounds have been injected into the main stream of the viscose and passed through the mixing apparatus which is customarily provided in such plants, they are already present in a completely uniform distribution.

It is also possible to employ smaller proportions of modified viscose without having the disadvantage of subsequently cleaning expensive pipe systems, which is a very time-consuming operation. This makes the production process more adaptable, for example, because it is easier to transfer from one type of fibre to another.

In addition to retarding coagulation and thereby influencing the formation of the thread in the viscose and in the spinning bath, the substances incorporated in the viscose in accordance with the present invention may have other effects which promote a satisfactory spinning process, owing to the presence of the polar sulphone groups in these substances. Examples of such additional effects are: The viscose may be easier to filter, the thread may be drawn to a greater extent, the spinnerets may be less liable to get blocked and these may be less incrustation of the spinnerets, the substances may have a clarifying effect on the spinning bath. This shows an improvement on the polyalkylene oxide compounds previously used. To improve the spinning process, it has been customary for a long time to add so-called "spinning oils," which are surface active products of various types. In the method used according to the invention, these spinning oils become superfluous.

The quantities of the above-described polysulphones that are added to the viscose vary according to the desired influence on the fibres and on the other conditions of the process, and lie between 0.1 and 4%, preferably 0.1 and 0.6% by weight.

The usual apparatus may be used for dosing without additional equipment.

The production of fibres, threads and films having improved mechanical properties by the claimed process is not confined to certain viscose compositions or compositions of the spinning bath, as already explained above.

However, the precipitating bath preferably contains at least 3% by weight of zinc sulphate. The stretching of the spun threads, which is necessary in order to obtain good textile properties, may be carried out by the known methods either in the spinning bath or in air or in special stretching baths.

The fibres and threads obtained with the above additives to viscose are distinguished from those produced without the use of these additives by having a flattened cross-section which may, for example, by kidney shaped, reduced swelling values and increased dry and wet tensile strength without reduced elongation at break.

The invention is further disclosed in the following examples which are illustrative but not limitative thereof.

Example 1

A viscose containing 7.2% cellulose and 5.5% total alkali, to which 1.8 g. of the compound described below has been added for each kilogram of viscose, was spun at a state of maturity corresponding to the salt point 8 from a spinneret having 48 apertures of 90μ cross section into an acid precipitating bath to produce a thread having a total denier to 180.

The bath contained 120 g./l. sulphuric acid, 230 g./l. sodium sulphate and 35 g./l. zinc sulphate and the temperature was 48° C. After leaving the spinning bath, in which it had traversed a length of 50 cm., the thread was stretched in air between 3 rollers by a total of 100%, the last roller having a drawing off speed of 36 m. per minute.

The material obtained was then collected in a spinning pot which revolved at 6000 revs. per minute, and the material was then deacidified and treated in the usual manner and dried under tension.

When comparing the textile data with those of a thread spun from a viscose without the addition of the above compound but otherwise the same, the following differences were found: the swelling was reduced by 27%, the dry tensile strength was about 22% higher and the wet tensile strength about 21% higher, and the elongation in the dry and wet state increased by 6.6 and 8.4% respectively.

This shows that the viscose additive can considerably improve the mechanical properties of the thread.

The polyether polysulphone which was used was prepared as follows: 1700 g. polyethylene glycol having a molecular weight 1700, 200 g. thiodiglycol and 12 g. orthophosphoric acid were heated in an atmosphere of CO_2 at 185° until the hydroxyl number had fallen below 30. Steam was blown through the reaction product for 4 hours at 120° and 15 mm. Hg pressure and then cooled to 80°. The polyether thioether obtained was then slowly treated with 340 g. hydrogen peroxide (32%) at 80 to 100°, and heating was then continued until no more hydrogen peroxide could be detected. The water was then distilled off in vacuo.

Example 2

1.9 g. of the compound described below was added per kilogram of viscose to a viscose with 7.0% cellulose and 4.6% alkali. The process was then carried out as described in Example 1 except that the precipitating bath was composed of 95 g./l. sulphuric acid, 215 g./l. sodium sulphate and 45 g./l. zinc sulphate and the temperature of the bath was 50° and the threads were stretched by 100% but only between two rollers.

On determining the textile data and comparing them with those of threads produced from viscose without additives, it was found that the swelling value was reduced by 35%, while the dry tensile strength and wet tensile strength were increased by 16% and 19% respectively.

The polyether polysulphone used was prepared as in Example 1 except that instead of using polyethylene glycol with a molecular weight of 1700, an equivalent quantity of oxyethylated butanediol-(1:4) having a molecular weight 800 was used.

Example 3

Observing the same conditions as in Example 1, 1.5 g. of the compound described below was used per kilogram of viscose, and the following improvements in the textile properties were obtained compared with the properties of unmodified viscose: reduction in swelling value, 32%; increase in dry tensile strength, 19%; increase in wet tensile strength, 22%.

The polyether polysulphone used was prepared as described in Example 1, except that the polyether thioether had a hydhoxyl number of 20 corresponding to a molecular weight of 5600.

We claim:

1. Viscose spinning solution which contains 0.1–4.0% by weight of a polyether sulphone compound containing one member of the group consisting of a sulfone group for every four carbon atoms in the polymer chain, an ether group for every four carbon atoms in the polymer chain and a sulfone group plus ether oxygen for every four carbon atoms in the polymer chain, said compound being soluble at least to the extent of 0.1% in 5% aqueous sodium hydroxide solution and having a molecular weight between 300 and 20,000.

2. Viscose spinning solution according to claim **1** which contains a polyether sulphone compound having at least one ether oxygen atom for every four carbon atoms.

3. Viscose spinning solution according to claim **1** which contains a polyether sulphone compound having at least one sulphone group for every four carbon atoms.

4. Viscose spinning solution containing 0.1 to 4.0% by weight of the viscose of a polyether sulphone having an average molecular weight of from 300 to 20,000 and at least one ether oxygen and one sulphone group for every four carbon atoms in the polymer chain, said polyether sulphone being soluble at least to the extent of 0.1 weight percent in a 5 weight percent aqueous sodium hydroxide solution.

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