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SOLUTIONS OF VINYL CHLORIDE POLYMER IN A MIXTURE OF TETRAHYDROFURANE AND A SOLVENT FROM THE GROUP CONSISTING OF SULFONE, SULFOXIDES, SULFONIC ACID ESTERS, AND SULFINIC ACID ESTERS

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The present invention relates to liquid compositions of matter, more especially solutions of polymers and/or copolymers of vinyl chloride, which can be spun to form threads and the like and which can be cast to form films. The invention relates further to the production of such compositions and to the production of spun filaments with the aid thereof.

It has been proposed in the literature to dissolve polyvinyl chloride in tetrahydrofurane and to work up these solutions into artificial threads. In this way, however, solutions are obtained of gluey consistency which in practice cannot be spun.

Attempts have been made to overcome this disadvantage by subjecting the polyvinyl chloride to an additional chlorination before dissolving it. This does give an increased solubility, for example even in acetone, but such a procedure means that the process involves an additional step.

Even when the spinning properties are improved by heating the solutions before spinning, for example to 50° C., and even when spinning is carried out at this temperature, a satisfactory result is not obtained. Moreover, when working in the vicinity of the boiling point of the solvent, bubbles are readily formed in the thread which considerably reduces its quality. The thread is also embrittled by spinning at raised temperature so that optimum strength values are no longer obtained upon subsequent stretching.

A whole series of lactones and lactams have been proposed in the patent literature which are said to be suitable as solvents for high polymers and copolymers of vinyl compounds. Such solvents or mixtures thereof, however, do not give solutions which can be used to spin threads of high quality.

In order to increase the solubility of polyvinyl chloride, certain quantities of other vinyl compounds have been added during polymerization. It has in fact been possible to increase the solubility of polyvinyl chloride in this way, but only at the cost of imparting inferior textile properties to the spun threads prepared therefrom.

A primary object of the present invention is the embodiment of spinning solutions which are free of the prior art defects as hereinbefore set forth. A further object of the invention is the preparation of spun polymeric or copolymeric vinyl chloride filaments of improved physical properties and manifestly superior textile properties, and which can be further conditioned to produce superior textile fibers. These objects are achieved in a simple way according to the present invention, with production of good spinning solutions of vinyl chloride polymers and copolymers from which high quality threads can be spun, by incorporating into the tetrahydrofurane, which is used as solvent, certain quantities of dimethylsulfoxide. The results thus achieved are surprising because neither tetrahydrofurane nor dimethylsulfoxide by itself gives vinyl chloride polymer solutions which can be satisfactorily spun. The favorable influence of dimethyl-sulfoxide becomes perceptible even on addition of about 10% by weight, relative to the weight of the solvent mixture, and increases with increasing quantity of the addition. The effect begins to diminish only when the dimethylsulfoxide becomes the predominant component of the mixture. A particularly favorable proportion of the two said compounds in the mixture is a proportion of one part by weight of dimethylsulfoxide to two parts by weight of tetrahydrofurane.

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Moreover, admixture with tetrahydrofurane according to the invention produces a fundamental change not only in the solvent power of dimethylsulfoxide but also in the solvent power of other solvents which have previously been proposed for polyacrylonitrile but which by themselves cannot be used to give vinyl chloride polymer solutions which can be satisfactorily spun. Such compounds which can be used with tetrahydrofurane as solvents to give vinyl chloride polymer solutions which can be satisfactorily spun according to this invention comprise other sulfoxides and other chemical compounds of analogous structure, as for instance sulfones, sulfonic acid esters, sulfinic acid esters and the like, such for example as:

Tetramethylenesulfoxide;
Pentamethylenesulfoxide;
Hexamethylenesulfoxide;
α-Methyl-trimethylenesulfoxide;
Trimethylenesulfoxide;
α-Methyl-tetramethylene-sulfoxide;
β-Methyl-tetramethylene-sulfoxide;
β-Keto-tetramethylene-sulfoxide;
Methane sulfonic acid methyl ester;
Methane sulfonic acid ethyl ester;
Methane disulfonic acid dimethyl ester;
Methane disulfonic acid diethyl ester;
Ethane-1,2-disulfonic acid diethyl ester;
Ethane-1,2-disulfonic acid dimethyl ester;
Butane-1,4-disulfonic acid dimethyl ester;
Propane-1,3-disulfonic acid dimethyl ester;
Chloromethane-disulfonic acid dimethyl ester;
Ethane sulfinic acid methyl ester;
Methane sulfinic acid ethyl ester;

Methane sulfinic acid methyl ester;
Dimethylsulfone;
β-Hydroxyethyl-methylsulfone;
Tetramethylenesulfone;
β-Methoxy-tetramethylenesulfone;
α-Methoxy-tetramethylenesulfone;
α-Methyl-tetramethylenesulfone;
β-Methyl-tetramethylenesulfone;
β-Hydroxy-tetramethylenesulfone;
α-Methyl-pentamethylenesulfone;
Hexamethylenesulfone;
β-Amino-tetramethylenesulfone;
β-Keto-tetramethylenesulfone;
β-Bromo-tetramethylenesulfone;
α-Methyl-trimethylenesulfone;
Pentamethylenesulfone;
Trimethylenesulfone;
α-Cyanomethyl-trimethylenesulfone; etc.

Preferably the solvent mixture contains from 10 to 50% by weight of the additional solvent. In certain circumstances the upper limit can be exceeded since even then a certain improvement in solubility is obtained.

The examples given below describe in more detail individual mixtures which have particularly good properties due to the nature and proportions of their ingredients.

When more than one of the said additional substances are admixed with tetrahydrofurane, which is possible according to the present invention, preferably the proportions of the ingredients are maintained within the above described limits, the total quantity of the additional substances lying within these limits.

The favorable effects in improving the solubility with the solvent mixtures used according to the invention are obtained not only with polyvinyl chloride but also with copolymers of vinyl chloride, for example vinyl chloride-vinyl acetate copolymers, vinyl chloride-vinylidene chloride copolymers, vinyl chloride-styrene copolymers, vinyl chloride-vinyl acetate-vinylidene chloride copolymers, etc.

One of the most important advantages of solutions produced according to the invention is that the solutions can be spun without difficulty at room temperature to form artificial threads, artificial bristles and the like, either by the wet spinning process or by the dry spinning process. In this way for example artificial threads are obtained with a strength of 2.5 to 3 grams/denier and extensions of 15–25%. The solutions are also very suitable for the production of films by casting. The solutions preferably contain from about 15 to about 25% by weight of polymer.

The following examples describe, solely by way of illustration, presently preferred embodiments of the process of the invention.

Example 1

200 parts by weight of polyvinyl chloride are introduced with stirring at 20° C. into a mixture of 150 parts by weight of dimethylsulfoxide and 600 parts by weight of tetrahydrofurane. The mixture is heated slowly to boiling while stirring and, when complete solution has been achieved, it is cooled again to about 20° C. The resultant solution can be spun, for example through multihole stainless steel jets, into water at 20° C.

Example 2

150 parts by weight of polyvinyl chloride are introduced with stirring at 20° C. into a mixture of 100 parts by weight of dimethylsulfone and 600 parts by weight of tetrahydrofurane. The

mixture is heated slowly to boiling while stirring and, when complete solution has been achieved, it is cooled again to about 20° C. The resultant solution can be spun into water at 20° C.

Example 3

300 parts by weight of polyvinyl chloride are introduced with stirring at 20° C. into a mixture of 250 parts by weight of tetramethylenesulfone and 750 parts by weight of tetrahydrofurane. The mixture is heated slowly to boiling while stirring and, when complete solution has been achieved, it is cooled again to about 20° C. The resultant solution can be spun into water at 20° C.

Example 4

150 parts by weight of a copolymer from equimolecular amounts of acrylonitrile and vinyl chloride are introduced with stirring at 20° C. into a mixture of 100 parts by weight of dimethylsulfone and 600 parts by weight of tetrahydrofurane. The mixture is heated until complete solution takes place, and is then cooled again to room temperature whereupon, after filtering if necessary, it may be spun into filament form, for example into water at 25° C.

Example 5

120 parts by weight of polyvinyl chloride are introduced with stirring at 20° C. into a mixture of 60 parts by weight of dimethylsulfone and 600 parts by weight of tetrahydrofurane. The mixture is heated and, when complete solution has been achieved, is cooled again to room temperature. The solution is then ready for use in the spinning of threads or in the casting of films.

Example 6

150 parts by weight of polyvinyl chloride are introduced with stirring at 20° C. into a mixture of 250 parts by weight of dimethylsulfoxide and 500 parts by weight of tetrahydrofurane, and the mixture heated. After complete solution has taken place, the solution is cooled to 20° C. and filtered, if necessary. It may then be converted into spun thread or cast film form.

Example 7

The procedure described in Example 5 is repeated, using 125 parts by weight of the polyvinyl chloride, 300 parts by weight of the dimethylsulfone, and 300 parts by weight of the tetrahydrofurane. The obtained solution may be spun into water at 25° C. or may be cast into film form.

The dimethylsulfone of Examples 4, 5 and 7 and the dimethylsulfoxide of Example 6 may, with equivalent results, be replaced by an equivalent amount of tetramethylenesulfoxide, hexamethylenesulfoxide or methane sulfinic acid methyl ester, while otherwise proceeding as described in the respective example.

Having thus disclosed the invention, what is claimed is:

1. A liquid composition of matter which can be spun to form threads and the like and which can be cast to form films, comprising a vinyl chloride polymer as solute in solution in tetrahydrofurane as solvent, said solvent having admixed therewith from about 10 to about 50% by weight of the mixture, of an additional solvent selected from the group consisting of sulfone, sulfoxides, sulfonic acid esters and sulfinic acid esters which can dissolve polyacrylonitrile completely but which do not by themselves give vinyl chloride polymer solutions which can be spun.

2. A liquid composition of matter which can be spun to form threads and the like and which can be cast to form films, comprising a vinyl chloride polymer as solute in a solution in tetrahydrofurane as solvent, said solvent having admixed therewith from about 10 to about 50% by weight of the mixture, of a sulfoxide.

3. A liquid composition of matter which can be spun to form threads and the like and which can be cast to form films, comprising a vinyl chloride polymer as solute in solution in tetrahydrofurane as solvent, said solvent having admixed therewith from about 10 to about 50% by weight of the mixture, of dimethylsulfoxide.

4. A liquid composition of matter which can be spun to form threads and the like and which can be cast to form films, comprising a vinyl chloride polymer as solute in solution in tetrahydrofurane as solvent, said solvent having admixed therewith an additional solvent selected from the group consisting of sulfone, sulfoxides, sulfonic acid esters and sulfinic acid esters, the

proportion between additional solvent and tetrahydrofurane in the solvent mixture being about 1:2 by weight.

5. A liquid composition of matter which can be spun to form threads and the like and which can be cast to form films, comprising a vinyl chloride polymer as solute in solution in tetrahydrofurane as solvent, said solvent having admixed therewith dimethylsulfoxide, the proportion between dimethylsulfoxide and tetrahydrofurane in the solvent mixture being about 1:2 by weight.

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JOHANNES KLEINE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,545,317	Stuchlik	Mar. 13, 1951