

The invention relates to a process for the preparation of mouldable solutions of cellulose in aqueous tertiary amine oxides from a suspension of cellulose in an aqueous solution of the tertiary amine oxide by the application of heat under reduced pressure.

Such a process is disclosed in PCT/WO Publication 83/04415, according to which cellulose is suspended in an aqueous solution of a tertiary amine oxide containing up to 40% by weight water and heated accompanied by agitation to temperatures between 90 and 120°C. At the same time the pressure is reduced to 80 to 150 mbar and water is drawn off until the cellulose passes into solution. In this way spinnable solutions containing up to 15% by weight water can be produced intermittently - i.e., in batches.

The shaping of said solutions in water produces films, filaments or shaped parts based on cellulose - i.e., articles which are nowadays produced on a large scale by the viscose process. However, where environmental safety is concerned, spinnable solutions of cellulose in aqueous tertiary amine oxides have a decisive advantage over viscose: although the tertiary amine oxide can be recovered during spinning and reused, the decomposition of viscose results in H_2S , COS , CS_2 and colloidal sulphur, substances which are expensive to dispose of.

A process of the kind specified is also known from French Patent A 2 450 293, according to Example 1 of which cellulose is mixed with an aqueous solution of a tertiary amine oxide in a mixer and

subjected to a negative pressure to evaporate water. The solution obtained is then supplied for further processing. This process also can be performed only intermittently.

It is also known from French Patent A 2 450 293 (Example 2) to mix cellulose with N-methyl-morpholine-N-oxide (NMMO) present in the solid form as a hydrate and containing 9.5% water, whereafter the solid dry mixture is melted. As a result, cellulose passes into solution, since the water content is already low enough. It can be gathered from the Publication "Cellulose-Amine Oxide Systems" in Carbohydrate Polymers, Vol. 2 (1982), No. 4, page 229, that for the dissolution of cellulose a water content of 17% must not be reached. According to Example 2 the solid mixture is melted in an extruder.

The aforementioned processes using tertiary amine oxides as solubilizers have hitherto not been widely adopted, since they still have a number of disadvantages.

It is true that processes using solid amine oxides (hydrates) as the starting material can be performed in extruders, the dissolution of the cellulose being started merely by the melting of the amine oxide hydrate, but such processes are expensive, since they require pure amine oxides. If, on the other hand, use is made of commercially available aqueous amine oxide solutions, correspondingly large quantities of water must previously be drawn off, something which is impossible in an extruder, since no high evaporation performances can be achieved. These processes are performed in agitator vessels.

However, due to the unfavourable surface-to-volume ratio of the liquid in the case of an agitator vessel water can be drawn off only with difficulty, the result being long dwell times in the range of 2 to 4 hours in the vessel. During that time the polymer cellulose chain is partially degraded, this being further promoted by the elevated temperature. This partial degradation in turn has an adverse effect on certain properties of the end products following the spinning process such as, for example, their strength, elongation and loop tenacity. It is also known that more particularly heating above 130°C may result in heavy discoloration due to the decomposition of the amine oxide used. In the case of certain compounds such as, for example, N-methyl-morpholine-N-oxide, the degradation may even take place explosively with a violent evolution of gas, so that due to the quantity in which they are present in the agitator vessel, the solutions may constitute a safety risk.

When the process is performed on a large industrial scale, therefore, with the use of agitator vessels operations must be performed suitably secured by high pressure autoclaves, which for economic reasons are out of the question for continuous operation. On the other hand, without a safety device only intermittent operation is possible in an agitator vessel, so that the process has very low flexibility, since parameters such as, for example, temperature and evaporation rate can be changed only with difficulty. There is also the fact that due to the high viscosity of the cellulose solutions, a great deal of the spinnable substance is retained by the agitator vessel, which makes it difficult to clean the vessel and further reduces the economics of the process.

It is an object of the invention to obviate these disadvantages and to provide a process for the preparation of cellulose solutions in aqueous tertiary amine oxides which can be performed continuously. The process according to the invention therefore uses as the starting substance not solid amino oxides, but an aqueous amine oxide solution. The heat treatment of the suspension is moreover substantially shorter according to the invention, to minimize the thermal stress on the cellulose and the tertiary amine oxide. Another object is to obviate the safety risk inherent in the prior art.

This problem is solved according to the invention by the features that in a process of the kind specified

- the suspension is continuously introduced via an inlet into an evacuable heatable vessel,
- the introduced suspension is spread mechanically in the form of a layer or film to form two surfaces,
- the spread suspension, for the supply of heat via a surface, is brought into contact with a heated inside wall of the vessel acting as a heating surface,
- the spread suspension is transported accompanied by intensive mixing over the heated inside wall,
- during transport over the heating surface the second surface of the spread suspension, remote from the inside wall, is subjected to the reduced pressure, to evaporate water until the suspended cellulose passes into solution, the water vapour being removed against the direction of transport of the suspension, and

- the mouldable cellulose solution is continuously drawn off from the vessel via an outlet.

The layer-like or film-like spreading of the cellulose suspension over the heating surface leads to a large liquid surface, which facilitates the removal of water. At the same time it makes possible the rapid heating of the suspension to the temperature required for the preparation of the solution. The transport over the heating surface achieves continuous mixing of the suspension, thus further accelerating the exchange of heat and substances.

The viscosity of the cellulose solution prepared according to the invention is between 50 and 15 000 Pa.s. To adjust the viscosity of the solution, which is measured in the relative system, and to influence the swelling behaviour of the cellulose in the suspension, a diluting agent such as, for example, ethanol, can be added to the suspension.

Particularly satisfactory mixing is achieved if the layer spread over the heating surface has a maximum thickness of 20 mm, preferably 1.5 to 5 mm.

Advantageously the tertiary amine oxide used is N-methyl-morpholine-N-oxide, preferably in an aqueous solution containing 40% by weight water.

A preferred embodiment of the process according to the invention is characterized in that the suspension is heated to a temperature between 50 and 150°C, preferably between 60 and

100°C, and subjected to a pressure of 0.5 mbar to 1000 mbar, preferably 50 mbar to 150 mbar.

It has been found to be particularly advantageous if the suspension is kept in contact with the heating surface for a duration of 1 minute to 60 minutes. On the one hand, this time is enough to produce a homogeneous solution, and on the other hand it is short enough to substantially prevent any decomposition of the tertiary amine oxide or degradation of the cellulose.

It has been found advantageous to perform the process according to the invention in an indirectly heated evacuable vessel having an agitating device and taking the form of a cylindrical tank having a centrally mounted agitator shaft and agitator vanes attached thereto, the radial distance between the agitator vanes and the inside wall of the tank being 20 mm at the most, and the upper portion of the tank comprising an inlet for the cellulose suspension and the lower end comprising an outlet for the mouldable cellulose solution.

In an advantageous embodiment of the apparatus used according to the invention, the agitator shaft has a distributing ring for spreading the cellulose suspension in a layer or film over the inside wall of the tank.

Advantageously to control the transport of the cellulose suspension along the inside wall of the tank the agitator vanes

have in relation to the axis of the agitator shaft an angle of inclination whose size is adjustable.

The process according to the invention, which can be performed with the apparatus used according to the invention, is extremely flexible as regards varying the operational parameters and involves a substantially lower safety risk than the prior art, since not a large quantity of solvent is heated at once, but only a comparatively small amount due to the spreading in the form of a layer over the heating surface.

The aforementioned apparatus used according to the invention will now be explained in greater detail with reference to Figs. 1 and 2, wherein:

Fig. 1 is a partial longitudinal section through the apparatus, and

Fig. 2 is a section, taken along the line II-II in Fig. 1, to an enlarged scale.

The reference 1 denotes the inside wall of a preferably vertical body of rotation which in the embodiment illustrated is constructed in the form of a tank 2 cylindrical over substantially its whole length. The majority of the inside wall 1 is enclosed in a heating jacket 3 having connections 4 and 5 for a heating medium, the connection 4 being used for the supply of the heating medium and the connection 5 for its removal.

An agitator shaft 7 having attached agitator vanes 8 and driven by a motor 6 is mounted centrally in the tank 2. The agitator vanes 8, which are flat in the embodiment illustrated, extend radially of the axis, their plane making an angle of inclination α to the axis 9 of the agitator shaft 7, the size of said angle being preferably adjustable. Disposed on the agitator shaft 7 above the agitator vanes 8 is a distributing ring 10 which spreads the cellulose suspension introduced via inlet 11 in a form of a layer on the side wall 1. The distributing ring 10 is therefore situated at the level of the inlet 11.

At its lower end the tank 2 tapers frustoconically and has an outlet 12 for the homogeneous cellulose solution. The agitator vanes 8 have a constant radial distance 13 from the inside wall 1 of the tank 2 over the whole extension thereof, such distance being 20 mm at most.

The upper portion of the tank 2 - i.e., above the plane of the distributing ring 10 - is formed with an opening 14 for the evacuation of the tank 2 and the drawing-off of water vapour.

The apparatus operates as follows:

The cellulose suspension, possibly a pre-heated condition, is continuously introduced via the inlet 11 into the tank 2, which is under reduced pressure, the suspension being caught at that place by the distributing ring 10, spread on the inside wall 1 and transported by the agitator vanes 8 along the indirectly

heated inside wall 1, acting as a heating surface, to the outlet 12 at the lower end of the tank 2. Heat-carrying media such as water, oil or steam are suitable for the indirect heating.

As the cellulose suspension is being transported along the indirectly heated inside wall 1, the suspension is heated, water evaporating at the same time due to the reduced pressure, so that the tertiary amine oxide is concentrated until the cellulose passes into solution.

Fig. 2 shows in detail how the cellulose suspension is processed in the tank 2. The drawing shows the agitator shaft 7 with agitator vanes 8, the inside wall 1 and the heating jacket 3, the direction of rotation of the agitator shaft 7 being assumed to be clockwise and indicated by arrow 7'. The layer-like spreading and the thickness of the layer of cellulose suspension is ensured by the radial distance 13 of the agitator vanes 8 from the heated inside wall 1. Due to the rotary movement, bow waves of cellulose suspension are formed on the agitator vanes, as illustrated diagrammatically in Fig. 2. As indicated in Fig. 2, the cellulose particles are circulated in the bow waves, this motion also being transmitted to the layer of suspension spread on the inside wall 1. This ensures a continuous relayering and intensive mixing of the suspension, which substantially encourages the exchange of heat and substance.

It is of decisive importance for the continuous performance of the process according to the invention that the separated water vapour is drawn off in counterflow in relation to the transport

of the suspension. It is also important to provide a large enough exhaust vapour space 15 for the drawing-off of the water vapour, such space being created if the length-to-diameter ratio of the cylindrical portion of the tank 2 has a value between 4 and 8.

The invention allows the production of cellulose solutions having up to 30% by weight cellulose.

The invention will be described in even greater detail in the following Examples.

Example 1:

A suspension of prehydrolysed cellulose sulphate (degree of polymerization approximately 1400) in an aqueous solution of N-methyl-morpholine-N-oxide having a water content of 40% by weight was heated to 70°C and continuously introduced in a quantity of 90 kg/h via inlet 11 into the apparatus according to the invention. The content of prehydrolysed cellulose sulphate in the suspension was so selected that after the evaporation of the excess water a final cellulose concentration of 10% by weight was obtained.

The agitator shaft was operated at a speed of 450 min⁻¹, the thickness of the layer spread over the inside wall 1 being 15 mm. The indirectly heated inside wall 1 had a surface of 0.5 m² and was so heated upon with heat carrying oil that a mean temperature difference of 83°C resulted in accordance with the heating of the suspension (in counterflow in relation to the heat-carrying oil). A pressure of 100 mbar was adjusted in the exhaust vapour space 15.

72 kg of homogeneous cellulose solution per hour could be obtained at the outlet 12, corresponding to a dwell time of the suspension in the apparatus according to the invention of 3 minutes. The solution could be removed in a degassed form, its viscosity being 1500 Pa.s (measured in the relative system). Microscopic investigation of the solution revealed that no undissolved cellulose particles were present in the solution.

The exhaust vapours formed were drawn off in counterflow at a temperature of 70°C and subsequently condensed, the flow of distillate being 29 kg per hour.

Example 2:

A suspension of ground prehydrolysed cellulose sulphate (degree of polymerization approximately 1400) in an aqueous solution of N-methyl-morpholine-N-oxide having a water content of 40% by weight was heated to 80°C and continuously introduced in a quantity of 90 kg/h via inlet 11 into the apparatus according to the invention. The content of prehydrolysed cellulose sulphate in the suspension was so selected that after the evaporation of the excess water a final cellulose concentration of 15% by weight was obtained.

The agitator shaft 7 was operated at a speed of 450 min⁻¹, the thickness of the layer spread over the inside wall 1 being 1.5 mm. The indirectly heated inside wall 1 had a surface of 0.5 m² and was so acted upon with heat-carrying oil that a mean temperature difference of 112°C resulted in accordance with the heating of the suspension (in counterflow in relation to the

heat-carrying oil). A pressure of 150 mbar was adjusted in the exhaust vapour space 15.

64 kg of homogeneous solution per hour could be obtained in a degassed form at the outlet 12. This flow of substance corresponded to a dwell time of 4 minutes.

The solution was obtained in the form of a highly viscous substance (11 000 Pa.s measured in the relative system), and no undissolved cellulose particles could be detected under the microscope. The solution was supplied directly to a spinning machine and spun into cellulosic fibres.

The exhaust vapours formed were drawn off in counterflow at a temperature of 80°C and subsequently condensed, the flow of distillate being 26 kg per hour.



1. A process for the preparation of mouldable solutions of cellulose in aqueous tertiary amine oxides from a suspension of cellulose in an aqueous solution of the tertiary amine oxide by the supply of heat at reduced pressure, characterized in that the suspension is continuously introduced via an inlet (11) into an evacuable heatable vessel (2); the introduced suspension is spread mechanically in the form of a layer or film to form two surfaces; the spread suspension is brought into contact for the supply of heat via a surface having a heated inside wall (1) of the vessel (2) acting as a heating surface; the spread suspension is transported accompanied by intensive mixing over the heated inside wall (1); during transport over the heating surface the second surface of the spread suspension, remote from the inside wall (1), is subjected to the reduced pressure, to evaporate water until the suspended cellulose passes into solution, the water vapour being removed against the direction of transport of the suspension; and the mouldable cellulose solution is continuously drawn off from the vessel (2) via an outlet (12).

2. A process according to claim 1, characterized in that the layer spread over the heating surface has a maximum thickness of 20 mm.

3. A process according to claim 2, characterized in that the spread layer has a thickness of between 1.5 and 5 mm.



4. A process according to one or more of claims 1 to 3, characterized in that the tertiary amine used is N-methyl-morpholine-N-oxide.
5. A process according to claim 4, characterized in that the tertiary amine used is N-methyl-morpholine-N-oxide in an aqueous solution with 40% by weight water.
6. A process according to one or more of claims 1 to 5, characterized in that the suspension is heated to a temperature between 50° and 150°C and subjected to a pressure of 0.5 mbar to 1000 mbar.
7. A process according to claim 6, characterized in that the suspension is heated to a temperature between 60 and 100°C and subjected to a pressure of 50 mbar to 150 mbar.
8. A process according to one or more of claims 1 to 7, characterized in that the duration of transport during which the suspension is in contact with the heating surface is 1 minute to 60 minutes.
9. Use of an apparatus for the performance of the process according to one of claims 1 to 8, having an indirectly heated, evacuable vessel (2) having an agitating device and taking the form of a cylindrical tank having a centrally mounted agitator shaft (7) and agitator vanes (8) attached thereto, the radial distance (13) between the agitator vanes (8) and the inside wall (1) of the tank (2) being 20 mm at the most, and the upper



portion of the tank comprises an inlet (11) for the cellulose suspension and the lower end comprises an outlet (12) for the mouldable cellulose solution.

10. Use according to claim 9, characterized in that the agitator shaft (7) has a distributing ring (10) for spreading the cellulose suspension in a layer or film over the inside wall (1) of the tank (2).

11. Use according to claim 9 or 10, characterized in that the agitator vanes (8) have in relation to the axis (9) of the agitator shaft (7) an angle of inclination (α) whose size is adjustable.