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LYOCELL FIBRES BASED ON DIRECT DISSOLUTION OF CELLULOSE IN N-METHYLMORPHOLINE N-OXIDE: DEVELOPMENT AND PROSPECTS

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The scientific principles of direct dissolution of cellulose in the NMMO—water system demonstrate the major possibility of obtaining concentrated spinning solutions and spinning hydrated cellulose fibres from them. The specific features of the properties of NMMO (high boiling point and insufficient thermal stability) that dissolves the NMMO—water system (narrow concentration range, optimum for dissolution of cellulose) makes it necessary to recycle the washing water by evaporating it, which causes high power consumption for this process. It is expedient to examine the possibilities of membrane technologies, including electrodialysis, for solving problems of recycling the solvent and cutting power consumption. However, this path only allows partially concentrating used washing water, since there is the danger of crystallization of NMMO di- and monohydrate. Spinning through an air gap from highly viscous solutions with long relaxation times at high spinneret draw ratios results in highly oriented fibres with high tensile rigidity (high deformation modulus). Fabrication of fibres whose properties correspond to ordinary viscose fibres will perhaps require "going away" from highly viscous solutions to a lower concentration and spinning by the ordinary wet method, but the volume of solvent used increases significantly, recycling it is more difficult, and power consumption increases. For the same reason of high orientation, the fibres exhibit important fibrillation when wet, and a "peach skin" effect is formed in the finished textiles. To reduce fibrillation, special treatments of the fabrics must be used, biofinishing, for example. During use of the articles, fibrillation can reappear, in laundering, for example. The technology for fabricating fibres of the Lyocell type requires solving many problems. Developing research on selecting alternative solvents and dissolving systems for direct dissolution of cellulose to obtain concentrated spinning solutions is simultaneously useful.

An important part of the scientific and engineering legacy of A. I. Meos is dedicated to cellulose and cellulose fibres. In his lectures to students on man-made fibre technology, he spoke of the dream of researchers of "finding a direct solvent of cellulose practically suitable for creating technology for fabrication of hydrated cellulose fibres." This dream came true, but only after he was no longer with us.

Direct dissolution of cellulose to obtain concentrated solutions and spin fibres and films from them has been the object of research to develop the corresponding technologies for many years. The extremely tempting conversion to technologies with direct dissolution of cellulose could allow reducing consumption of chemicals by ten times in comparison to consumption in viscose and cuprammonium processes, facilitating recycling, and decreasing and improving the cleanness of harmful industrial discharges. Attempts to reach these goals have been examined in many publications [1-10].

Many substances have been tested as solvents of cellulose:

– caustic soda solution, which causes significant swelling of cellulose and dissolves it, but only at a maximum degree of polymerization (DP) of 150-200; such a DP is totally insufficient for manufacturing fibres;

– zinc chloride solution of 65% concentration, which allows obtaining sufficiently concentrated solutions of cellulose; this process could not be developed due to its rapid breakdown;

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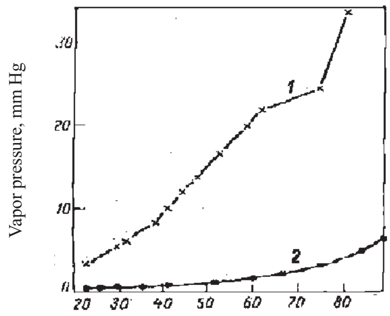


Fig.1

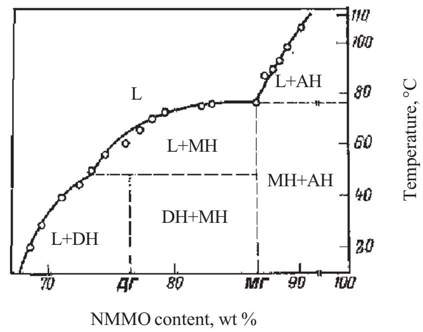


Fig.2

Fig. 1. Vapor pressure as a function of temperature: 1) monohydrate (13.5% water); 2) dehydrated NMMO.

Fig. 2. Phase diagram of NMMO—water system. Regions of existence of: L — liquid; L + DH — liquid + dihydrate; L + MH — liquid + monohydrate; DH + MH — dihydrate + monohydrate; L + AH — liquid + anhydrous crystals; MH + AH — monohydrate + anhydrous crystals.

– saturated sodium thiocyanate solution, which causes strong swelling of cellulose but does not allow obtaining concentrated solutions;

– solutions of polyvalent metal complexes, which also cause swelling and dissolution of cellulose, but the use of these substances is restricted by the insufficient DP of cellulose; the best results are obtained in dissolving cellulose in cadoxen and SITA (sodium-iron tartaric acid solution), but this method of dissolution has also not fulfilled hopes;

– different N-amino oxides and other organic compounds; however, the dissolution conditions and properties of the solutions, as well as the properties of the solvents themselves, were technologically and economically unacceptable.

As a result of the studies conducted by many scientists, including in our country, in the 1980s-1990s, it became clear that the process based on use of N-methyl N-oxides as the solvent could be a possible technology for direct dissolution of cellulose and spinning of hydrated cellulose fibres.

The advances of many firms and research organizations in creating alternative methods of obtaining hydrated cellulose fibres based on direct dissolution of cellulose without chemical transformations allowed finding a promising version of this process. Thanks to these advances, the scientific principles of direct dissolution of cellulose were created, using N-methylmorpholine N-oxide (NMMO) as the most promising solvent and spinning fibres from the solutions obtained.

In discussing the history of this process, several fundamental dates should be mentioned:

– 1936-1939 — a method of direct dissolution of cellulose in amino oxides was proposed [Ch. Granacher and R. Sallmann, DR Pat. No 713486 (1936); US Patent No. 2179181 (1939)];

– 1966-1969 — use of NMMO—water mixture as a solvent of cellulose for manufacturing fibres was proposed [D.-L. Johnson, US Patent No. 3447939 (1969); Brit. Patent No. 1144048 (1969)];

– 1979 — research and development began on fabrication of a new kind of hydrated cellulose fibre by Courtauld in Great Britain; the fibre as called "Tencel;"

– 1983-1984 — a pilot unit was constructed for fabricating Tencel staple fibre in Coventry, Great Britain, and commercial production was begun;

– 1988 — industrial production of Tencel fibres began in Grimsby, Great Britain;

– 1989 — the specific name "Lyocell" was given to hydrated cellulose fibres made by direct dissolution of cellulose in N-amino oxides;

– 1990 — pilot production of Lyocell fibres by direct dissolution of cellulose in an aqueous solution of NMMO was created by Lenzing in Austria;

– 1992 — production of Tencel fibres by Courtauld began in Mobile, Ala. USA;

– 1992-1994 — research on Lyocell fibres began at the Textile and Man-Made Fibre Research Institute in Rudolstadt and was subsequently organized by Alceru Schwarza GmbH; the fibre was called "Alceru;"

– 1993-1997 — an industrial Lyocell plant was built and started up by Lenzing in Heiligenkreuz, Austria;

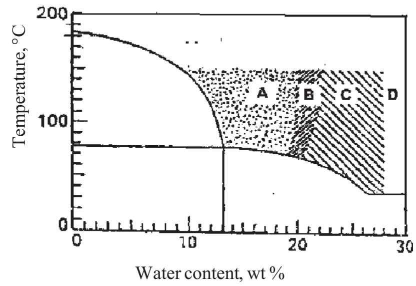


Fig. 3. Regions of reaction of the NMMO—water—
—cellulose system: A) compatibility (solubility); B, C)
irreversible swelling; D) no visible reaction.

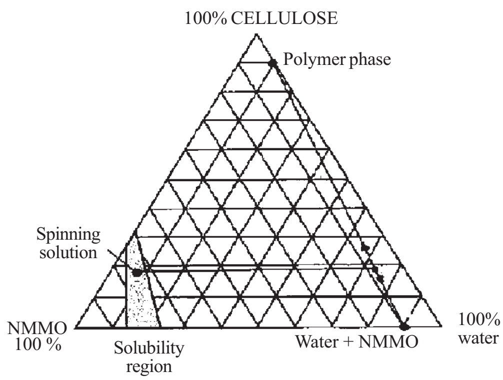


Fig. 4. NMMO—water—cellulose phase diagram in preparation of
spinning solution and spinning fibres

– 1996 — Courtauld (part of Acordis) expanded production of Tencel fibres in Mobile, USA;

– 1998 - a pilot plant for production of Alceru fibre based on direct dissolution of cellulose in an aqueous solution of NMMO was created by Alceru Schwarza;

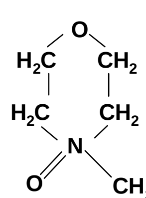
– 1998 — industrial production of Tencel fibres was expanded by Courtauld in Grimsby.

The total production capacity for fibres of the Lyocell type is now estimated at 150-180,000 tons [11]. There are no published data on their real production volume.

The theoretical principles of this process have been generalized and analyzed in detail in the literature. In contrast, the engineering problems have been generalized very little, and ways of solving the complex process problems have been inadequately analyzed. The present publication concerns these aspects. Let us examine the present status of direct dissolution of cellulose in the most promising system based on NMMO—water mixtures and the technology for fabricating fibres from these solutions.

BASIC PROPERTIES OF N-METHYLMORPHOLINE N-OXIDE, THE NMMO—WATER AND NMMO—WATER—CELLULOSE SYSTEMS

The basic properties of NMMO have been sufficiently examined in the literature [12-14]. Its chemical formula is



The molecular weight of $C_5H_{11}N_2O$ is equal to 115.2; the melting point (anhydrous NMMO) is 170°C, the saturated vapor pressure is 0.35 mm Hg at 25°C, 6.5 mm Hg at 91°C; the initial decomposition temperature is ≥100-110°C, and the intensive (turbulent) decomposition temperature is ≥130-140°C. NMMO is hygroscopic and forms hydrates.

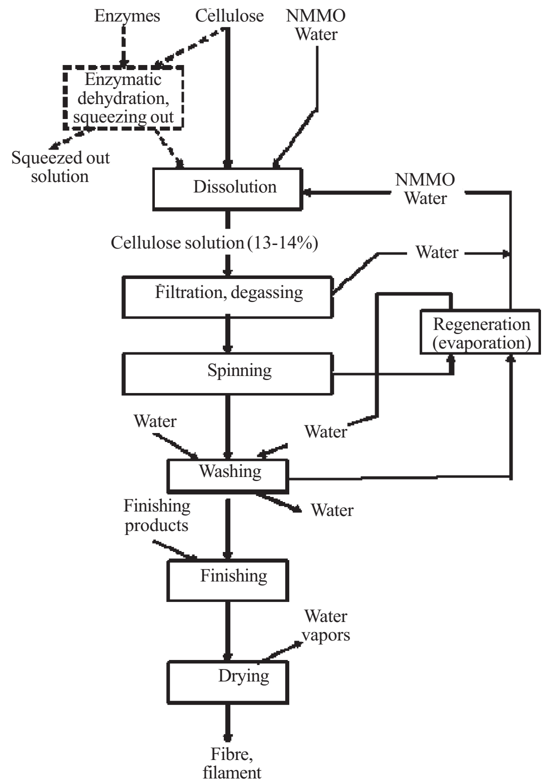


Fig. 5. Diagram of manufacture of Lyocell fibres. The version of the process with preliminary dehydration of cellulose is indicated by the hatched lines.

The monohydrate $C_5H_{11}N_2 \cdot H_2O$ contains 13.5 wt. % water, t_m = 74-78°C; the dihydrate $C_5H_{11}N_2O \cdot 2H_2O$ contains 23.5 wt. % water, t_m = 38-39°C. The dependence of the vapor pressure of NMMO and its monohydrate on the temperature is shown in Fig. 1.

The phase diagram of the NMMO—water system shown in Fig. 2 is very important for examining the technology and recycling of the solvent.

An examination of the different reaction regions of the NMMO—water—cellulose system (Fig. 3) and the NMMO——water—cellulose phase diagram (Fig. 4) are very important for selecting the optimum spinning solution composition and conditions of preparation and optimizing the fibre-spinning conditions.

OVERALL PROCESS SCHEME FOR PRODUCTION OF SPINNING SOLUTIONS AND SPINNING FIBRES

The basic stages of dissolution, preparation of solutions, spinning, washing, and drying the fibres are shown in Fig. 5 [17-31]. Let us examine the basic stages of this manufacturing process.

The DP of the initial cellulose is within 500-800. At too high DP, it undergoes degradation with adjustable enzymatic hydrolysis or by catalytic oxidation in the presence of hydrogen peroxide, cobalt compounds, or other catalysts. This process is similar to the process used in viscose technology.

Due to the high viscosity of the spinning solutions, powerful dissolving equipment with intensive stirring is used to prepare them. After preparation, the solution is degassed with simultaneous vacuum evaporation of water in a thin-layer vertical unit. The temperature of the solution is 90-110°C. The highly viscous spinning solution with a 15-18% concentration is filtered, measured with a metering pump, and goes to spinning.

List AG, Switzerland and Alceru Schwarza have developed a horizontal, two-screw unit (with intermittent screws) for preliminary mixing of cellulose with NMMO and a horizontal solvent degasser with a powerful drive (equipped with beaters and counterbeaters). The solution is degassed in vacuum evaporation of a small amount of water [32].

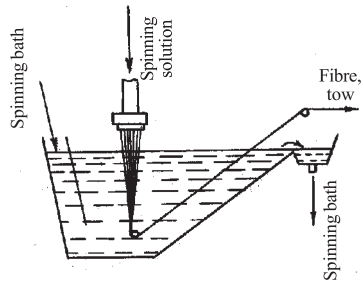


Fig. 6. Diagram of spinning fibres from NMMO—water—cellulose solutions through an air gap.

In production of staple fibres, block spinnerets designed for high pressure of the spinning solution are used. Spinning is conducted with the wet method through an air gap (dry-wet spinning) into an aqueous spinning bath containing NMMO at a speed of 75-100 mg/min and with higher spinneret drawing. A diagram of the fibre spinning process is shown in Fig. 6.

After spinning, the fibres can undergo plasticizing drawing (to obtain the high-strength fibres used for several industrial purposes, for example, for reinforcement of composites) and undergoes multiple counterflow washings in the form of tow.

Washing takes place continuously in a multisection unit with intermediate squeezing out between sections. The design of the washing unit, number of stages, and intensity of washing are most important for obtaining washing waters with the maximum concentration of solvent — NMMO. There can be 20 washing sections. One of the most intensive modern washing methods is multiple jet treatment of tow moved by a wide thin belt in each section by washing water at high pressure.

After washing, the tow (sliver) is crimped and cut to the desired length; the cut fibre is then washed again in cut form, then treated with a brightening solution and dried to the desired moisture content.

Other manufacturing and equipment solutions for treating flat tow (sliver) and its counterflow intensive water treatment (washing) for manufacturing the maximally concentrated washing water with respect to NMMO content are also possible.

SCHEME FOR MANUFACTURING LYOCELL FIBRES BY THE SOLID-PHASE METHOD

A new manufacturing scheme for Lyocell (Orcel) fibres using original technology of preliminary formation of the NMMO—water—cellulose solid-phase system with a concentration of under 25% was developed at the All-Russian Scientific-Research Institute of Polymer Fibres [33, 34]. This scheme is shown in Fig. 7.

REGENERATION OF THE SOLVENT — NMMO

The technical possibilities for recycling the solvent have now been found. In production of Lyocell fibres, it was possible to minimize the specific consumption of NMMO to 0.01-0.03 kg/kg for staple fibre and 0.03-0.05 kg/kg for thread.

Since the NMMO—water system is the cellulose solvent, recycling is not a simple problem in consideration of the properties of the system and the NMMO itself reported above [24]. The recycling problem is far from completely solved and the economics is also far from completely solved.

Recycling of the solvent consists of two stages; ion-exchange removal of contaminants and evaporation of water.

The ion-exchange process includes treating the solution with cation- and anion-exchange resins, which is necessary to remove destabilizing contaminants and for bleaching.

The washing water is evaporated. The water vapors are condensed, and the condensate formed is used again for washing the spun fibre. The aqueous solution of NMMO with the required concentration that remains in the bottoms is returned to the beginning of the process for dissolving the cellulose and making the spinning solution. Evaporating a large amount of water from the washing waters causes high power consumption and for this reason is a large item in the costs and correspondingly the price of Lyocell fibres.

At high temperatures, NMMO decomposes with formation of N-methylmorpholine and other amines. For this reason, propyl gallate is added to the dissolving system as an antioxidant-stabilizer.

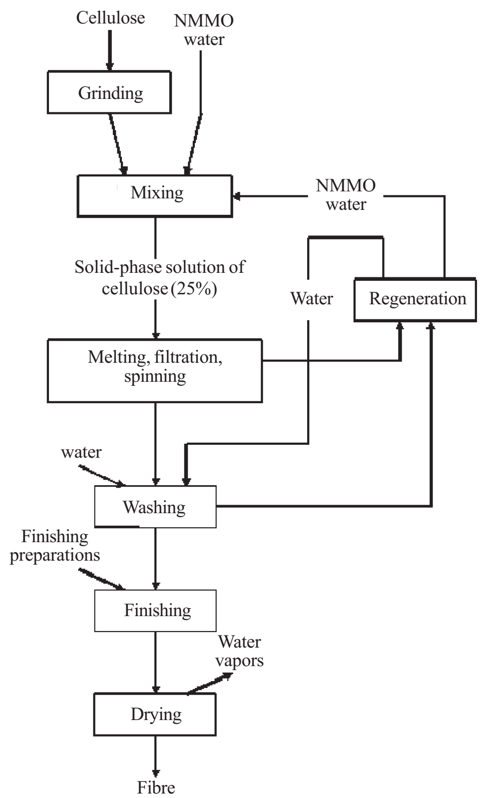


Fig. 7. Diagram of solid-phase production of Lyocell (Orcel®) fibres.

In all processes related to high-temperature treatment with NMMO, it is necessary to avoid heating it above 120°C to exclude intensive (close to explosive) exothermic decomposition. For this reason, reliable monitoring and regulation of the temperature conditions must be organized.

The manufacturing scheme with evaporation of all of the washing water is very power-consuming. For this reason, improvement of the washing stage with minimization of consumption of washing water and maximum concentration of NMMO is an important problem in development of the Lyocell process. High power consumption thus became the reason why development of Lyocell fibre technology stopped.

The problem of minimizing the amount of washing waters and increasing the concentration of NMMO in them in production of Lyocell fibres is even more complicated. The creation of effective counterflow in washing them after spinning has not been possible, so that production of Lyocell fibres is not very profitable and is still not being developed.

SOME FEATURES OF THE STRUCTURE AND PROPERTIES OF FIBRES OF THE LYOCELL TYPE

The properties of fibres of the Lyocell type in comparison to the properties of other fibres are examined in detail in the literature [17-31, 33, 34].

The high concentration and high viscosity of the spinning solution are a necessary condition for stable spinning of fibres through an air gap, since they undergo high spinneret drawing in the air gap.

Cellulose is a rigid-chain polymer (its statistical segment is equal to approximately 10 nm). The high concentration and high viscosity of the cellulose solution causes the appearance of high orientation of its macromolecules in a transverse velocity gradient field in flowing into the spinneret holes. Such spinning conditions lead to the very restricted occurrence of relaxation and disorientation processes while preserving high molecular orientation in the spun fibre. It is still not possible to obtain moderately oriented fibres with such technology, which significantly narrows the assortment of Lyocell fibres by allowing production of fibres with relatively high mechanical properties alone.

The properties of Lyocell fibres are compared with the properties of other kinds of cellulose fibres in Table 1. The data in Table 1 indicate that high orientation leads to marked rigidity of the fibres (low deformability and high deformation modulus). These indexes of Lyocell fibres are much higher than for ordinary viscose fibres and even higher than for viscose high-modulus fibres (Siblon type, modal in Western terminology).

The high ordering of the structure causes marked fibrillation of wet Lyocell fibres, and this also limits the assortment. The fibrillation effect makes it necessary to use special treatments of fabrics made of Lyocell fibres [17-29, 35]. The character of fibrillation based on manufacturers' data is shown in Fig. 8.

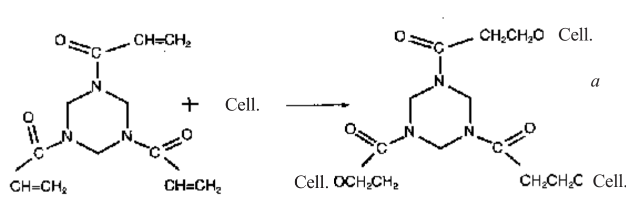
The evaluation of the level of fibrillation of different kinds of hydrated cellulose fibres shown in Fig. 9, based on Lenzing data [17-29], shows both the attained level of minimization of the phenomenon and the future (desired) level. Improving the Lyocell fibre production process will allow hoping for a further decrease in fibrillation, but this problem has not yet been completely solved.

METHODS OF REDUCING FIBRILLATION

Decreasing fibrillation of Lyocell fibres is very pressing for expanding the areas of their application. It has been the subject of many studies and development of many methods [17-31, 35-38]. The basic proposals for solving this problem can be combined in several groups:

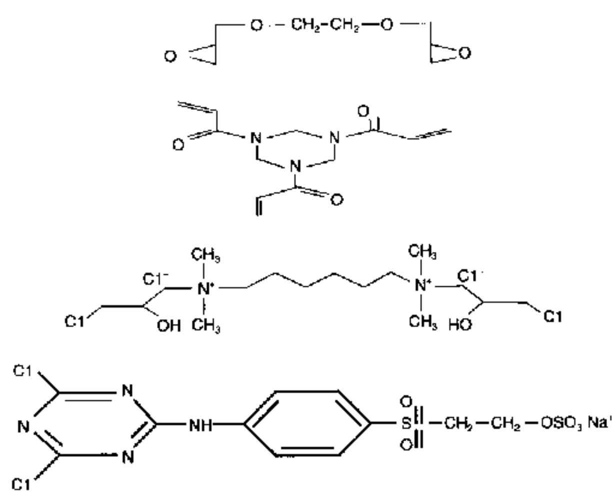
– optimization of the spinning conditions which reduces fibrillation to some degree;

– crosslinking treatments of as-spun fibres before drying; this method requires adding special stages to the technology and involves use and recycling of additional chemicals or treatment of discharges [24, 37, 38]; for example, crosslinking treatment with trisacrylamido-trihydrotriazine (reaction scheme *a*) or other polyfunctional compounds and condensation products (oligomers):



a

– use of crosslinking treatments in finishing fabrics made of Lyocell-type fibres; some products used for crosslinking treatments of hydrated cellulose fibres and used for Lyocell fibres are shown below [24, 37]:



a

b

d

e

the crosslinking agents shown here are the following: *b* — ethylene glycol diglycidyl ether; *c* — trisacrylamido-trihydrotriazine (AXIS); *d* — bistrihydroxychloropropyl-N,N-tetramethylhexamethylenediamine (CATIONON); *e* — Subatex AD 4425; crosslinks are formed in basic medium (AXIS, Cybatex AE 4425) or in heat treatment before or after dyeing;

TABLE 1. Comparison of the Structure and Properties of Different Kinds of Cellulose Fibres

Indexes	**Lyocell**	Viscose fibres		Cotton	Flax
		ordinary	high-modulus		
Composition, %					
cellulose	100	100	100	97 - 98	80 - 85
lignin				–	3 - 5
Shape of fibrils	Drawn	Drawn	Drawn	Spiral	Spiral
Tilt of fibrils, deg.	8 - 10	10 - 20	8 -10	25 - 45	3 - 10
Moisture content,* %	11 - 13	13 - 14	12 - 13.5	7 - 9	10 - 13
Strength,* cN/tex	35 - 47	20 - 26	32 - 36	25 - 40	40 - 55
Preservation of strength, %					
loop	30 - 40	30 - 40	20 - 30	45 - 65	–
wet	60 - 80	50 - 55	60 - 70	105 - 110	100 - 105
Elongation,* %	11 - 16	18 - 25	12 - 15	8 - 10	2 - 3
Deformation modulus,* GPa	8 - 10	3 - 5	5 - 6.5	5 - 9	30 - 50
Deformation modulus in wet state, GPa	3 - 4.5	0.6 - 1	1.5 - 2	–	–

*In standard conditions.

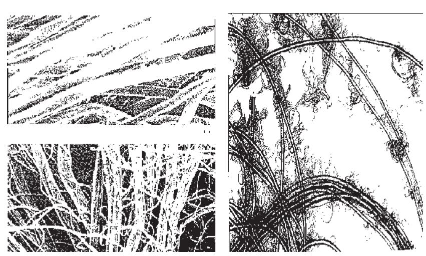


Fig.8

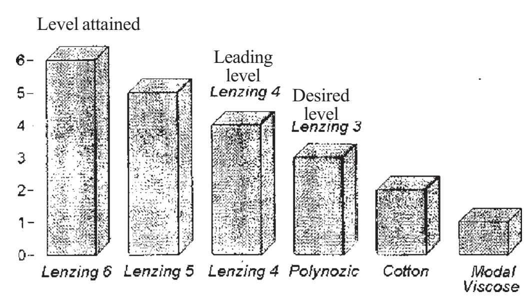


Fig.9

Fig. 8. View of fibrillated Lyocell fibres.

Fig. 9. Level of fibrillation of different kinds of hydrated cellulose fibres.

– treatments with products, melamine—formaldehyde derivatives, for example, used to give dimensional stability (reduced wrinkling) to fabrics made from cellulose fibres can be used; however, such treatments can lead to sanitary-hygienic restrictions on use of the fabrics due to gradual liberation of formaldehyde; formaldehyde-free methods of crosslinking finishing are preferred;

– "fine" biofinishing of fabrics using enzymatic preparations; in such "delicate" finishing, relatively thick fibres are damaged very little, while thin separated fibrils degrade relatively rapidly; however, such treatment reduces the strength characteristics of the fibres and does not protect fabrics and articles from repeated fibrillation during use (especially in laundering and other effects of water).

PROSPECTS FOR LYOCELL FIBRES

Direct dissolution of cellulose in the NMMO—water system and production of concentrated spinning solutions and high-speed wet spinning through an air gap ("dry-wet spinning") ensures high output of the processing equipment and the entire process of manufacturing Lyocell fibres.

The method of direct dissolution of cellulose allows reducing consumption of chemicals by several hundred times in comparison to the viscose process. The specific consumption of solvent — NMMO — varies from 0.01 to 0.03 kg/kg of fiber according to the different data. However, recovery of NMMO causes important difficulties as this is done by evaporation and subsequent evaporation of water.

The narrow region of solubility of cellulose, which can be seen in the NMMO—water—cellulose phase diagram, is the determining manufacturing difficulty (see Fig. 4). The occurrence of thermal decomposition of NMMO during preparation of the spinning solutions at 90-110°C and the danger of intensive exothermic decomposition at temperatures above 130°C should also be noted.

Manufacture of Lyocell fibres, together with the important advantages, is thus technologically complex, which makes it difficult to develop their production. Although the solvent recycling problems have been technically solved, evaporating the water from washing waters requires important power consumption which significantly reduces production efficiency. For this reason, reducing water consumption for washing is very urgent and requires use of a highly efficient counterflow scheme for this process.

The important difficulties in production of Lyocell fibres are due to the high consumption of washing water and the possibility of manufacturing highly oriented fibres alone. Manufacturing only fibres of high linear density for industrial applications is thus potentially expedient. The difficulties in recycling the solvent — NMMO — in production of Lyocell fibres are due to the high washing water consumption and the lower concentration of washing waters going to recycling. These difficulties increase with a decrease in the linear density of the fibres.

In the further development of Lyocell fibre production technology, significant improvement of recycling of process liquids and washing water is required, as this would allow minimizing power consumption. The use of new recycling methods such as membrane technologies, electrodialysis, etc., to remove water from the washing waters is difficult due to possible separation of NMMO hydrates. However, membrane concentration of these waters before evaporation to a level that guarantees formation of crystal hydrates is possible.

As examined above, due to the specific features of the properties of concentrated spinning solutions and dry-wet spinning through an air gap, high orientation and the related high rigidity and fibrillation in the wet state and, as one of the consequences, reduced wear resistance of fabrics and articles during use, are characteristic of Lyocell fibres. Although these features have now been partially overcome, it is still difficult to eliminate them totally.

In further development of Lyocell fibre technology, the features and difficulties listed above will probably be eliminated to a significant degree. However, they will still restrict the area of application of Lyocell fibres in comparison to the area of application of traditional viscose fibres. As a result, Lyocell fibres or textiles made from them will require special finishing.

The capacity for fibrillation in Lyocell fibres can be utilized in some types of materials: textiles and articles with a "peach skin" surface, in production of special kinds of filtering nonwoven materials, in production of paper and other fibre materials.

Production of modified Lyocell fibres has certain prospects. Alceru Schwarza and Zimmer are development production of flameproof and antimicrobial varieties and fibres with new physical and physicochemical properties.

The niche occupied by Lyocell fibres thus differs from the niche for viscose fibres. The further development of Lyocell fibre technologies will be aimed at reducing their inherent drawbacks and correspondingly improving their functional properties and expanding the assortment and areas of application.

Manufacture of fibres of the Lyocell type is still developing slowly and there is no information on construction of new plants. Nevertheless, Lenzing has announced a 20,000 ton increase in production capacity.

In summarizing this examination of the prospects for production of fibres of the Lyocell type, we note that they are gradually "gaining their place in the sun" and will probably develop in the future.

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