

THE INFLUENCE OF PULP RESIN ON THE PROPERTIES OF HWM-FIBRES

INGEMAR CROON, HEIMER JONSÉN and HANS-GUNNAR OLOFSSON

Mo och Domsjö AB, Research Laboratory, Örnsköldsvik, Sweden

INTRODUCTION

For commercial production of HWM-fibres both sulphite and prehydrolysis sulphate pulps are used nowadays. These two main groups consist of a range of pulps, varying in the wood raw material used, degree of refinement, viscosity, etc.

Sulphite and sulphate cooks are carried out under completely different conditions, and the pulps obtained by the two processes show characteristic properties. This interesting topic has been the subject of several investigations. Most authors agree that the main difference in behaviour of sulphite and prehydrolysed sulphate pulps is due to the difference in the physical state of the polysaccharides in the fibres. In sulphate pulp fibres the polysaccharides have a higher degree of order.

The pulps produced by these two main processes have also different resin contents. (In this paper content of resin means the material which may be extracted from the pulp using dichloromethane as solvent.) During the alkaline sulphate cook, the main part of the resin is saponified, dispersed in the black liquor and finally removed from the pulp in the washing operation. The prehydrolysed softwood pulps which today are used for qualified products (cord and HWM-fibres) consequently have a very low resin content (<0.05 per cent). Resin is claimed to have a beneficial influence on the viscose process since it gives improved filterability, milkiness, etc, but the absence of resin in this type of pulp is compensated by the addition of synthetic surface active agents.

Because of the beneficial influence of the resin on filterability and milkiness it is often stated that the sulphite pulps for the preparation of conventional rayon products should contain resin in the range 0.20–0.35 per cent. Different rayon producers specify on their pulp purchase somewhat differing values within this range depending on their process conditions and hypotheses. However, as is later going to be shown, the hydrophobic part of the resin causes such aggravating difficulties in the viscose process that the presence of resin in dissolving pulp is highly questionable.

RESIN IN BLEACHED SULPHITE DISSOLVING PULPS

During a sulphite cook of well stored spruce wood about 60–70 per cent of the resin is removed. The dissolved material consists mainly of hydrophilic substances (resin acids and free oxidized fatty acids) and some dispersed hydrophobic compounds. The resin in the unbleached pulp contains

mostly fatty acid esters of glycerol, terpene and fatty alcohols and sterols, together with unoxidized fatty acids, fatty and terpene alcohols and hydrocarbons. Depending on the duration of storage of the wood, the amount of unsaturated substances in the resin varies.

In Scandinavia, dissolving pulps are today usually bleached by a sequence based on chlorination, alkali extraction and treatment with chlorine dioxide and hypochlorite. Treatment of the pulp with chlorine in the first bleaching stage results in the addition of chlorine to many of the compounds in the resin. A sticky material is then formed which is difficult to remove in the subsequent bleaching stages, where, the resin is further modified by saponification and complex oxidation reactions. Consequently the resin in the finished pulp has an extremely complicated composition (several hundred compounds). It consists mostly of fatty acid esters such as glycerides, fatty alcohol esters and sterol (terpene) esters together with hydrocarbons, fatty alcohols, sterols (terpene alcohols) and fatty acids (*Figures 1 and 2*). Many of these substances have a high chlorine content. The resin as a whole has a chlorine content of about 15 per cent.

INFLUENCE OF THE RESIN ON THE VISCOSE PROCESS

It has already been mentioned that the resin has some beneficial effects on the viscose process but the detrimental effects are very significant. The hydrophobic part of the resin accumulates in the foam of the deaerators. As these compounds have a tendency to solidify they may form deposits in the equipment and tubes. In such deposits we have identified saturated and unsaturated hydrocarbons, chlorinated fatty acid esters of fatty alcohols, sterols, terpene alcohols as well as free alcohols and acids (*Figure 3*). Similar compounds have also been identified in deposits on spinning jets proving that a part of such deposits arises from the resin.

INFLUENCE OF RESIN ON THE FINISHED HWM-FIBRES

Between 30 and 50 per cent of the resin is dissolved during the steeping; thus a large part of the resin in the pulp reappears in the viscose and later in the yarn. The part of the resin which is precipitated in one or the other

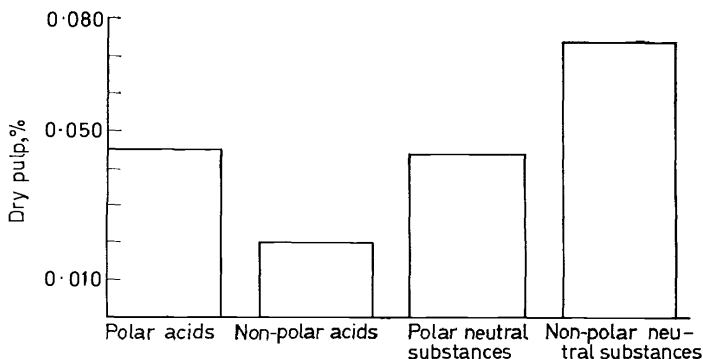


Figure 1. Fractionation of resin in polar and non-polar acids and neutral substances

INFLUENCE OF PULP RESIN ON PROPERTIES OF HWM-FIBRES

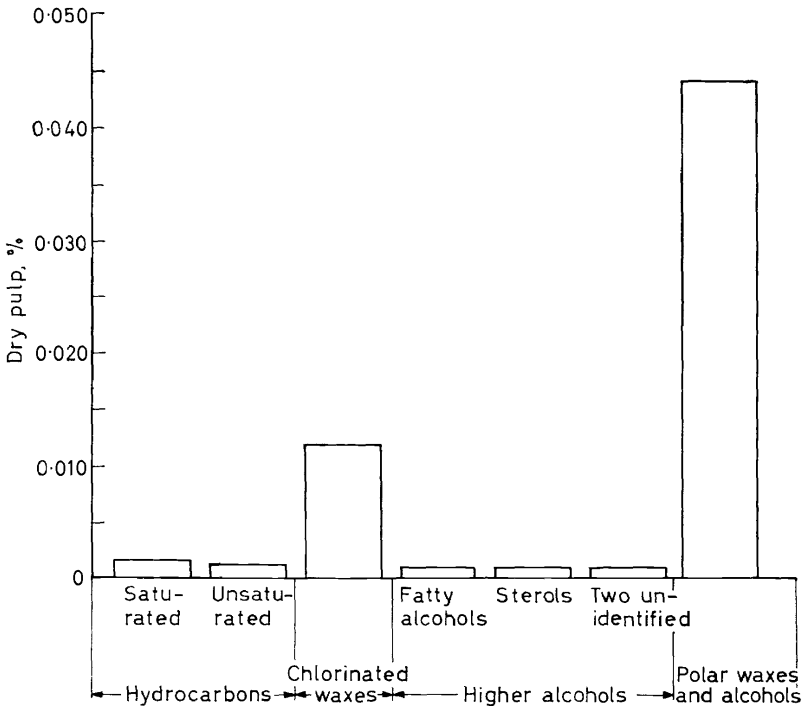


Figure 2. Fractionation of the non-polar part of resin from a dissolving pulp

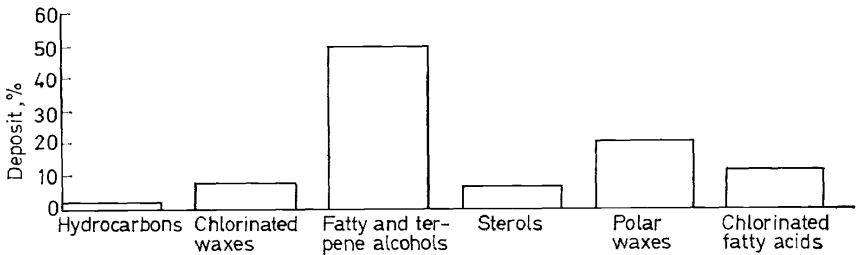


Figure 3. Composition of resins from deposits in a deaerator

form during the viscose preparation is very difficult to disperse and will be present in the viscose in the form of undissolved particles. These particles may cause weaknesses in the yarn and result in uneven spinning and variable yarn strength. The resin particles furthermore dissolve carbon disulphide which during drying of the filaments expands, giving rise to bubbles and inflated cross-sections.

STRENGTH AND ELONGATION

We have spun staple fibre from two standard spruce pulps with very different resin content, 0.53 and 0.12 per cent respectively. The staple fibres obtained had resin contents of 0.26 and 0.05 per cent respectively.

The two samples turned out to have quite different heat stability properties which is apparent from *Figure 4*.

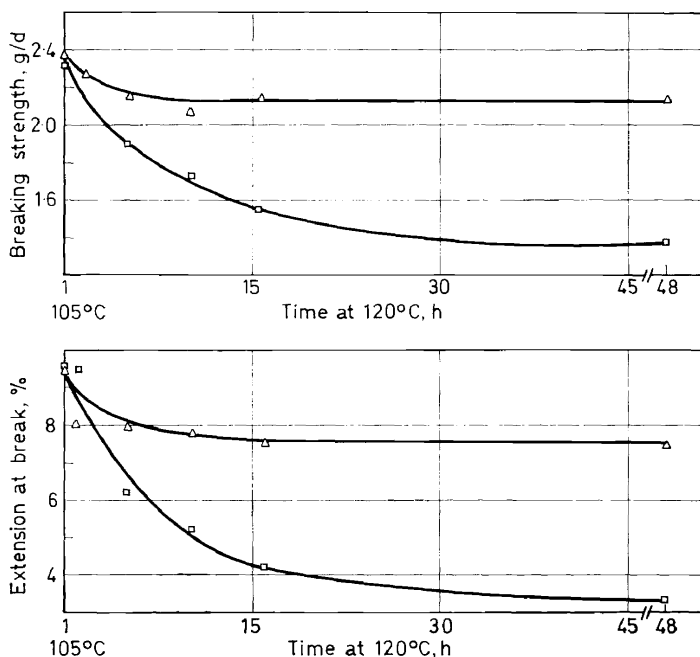


Figure 4. Heat stability of rayon produced from standard pulps [\triangle — \triangle , Resin in the pulp and silk 0.12 and 0.05 per cent; \square — \square , Resin in the pulp and silk 0.53 and 0.26 per cent respectively]

The thread with the high resin content (0.26 per cent) was substantially degraded so that after treatment for 16 h at 120°C less than 80 per cent of the original tensile strength and hardly 75 per cent of the elongation were left. The thread with the low resin content on the other hand was essentially unchanged even after 48 h at 120°C. Tests carried out at various temperatures showed that the thread from the high resin pulp was greatly degraded already between 105–120°C (*Figure 5*).

On our laboratory spinning machine, HWM-fibres were spun (according to the Toramomen procedure) from two different pulps, one American prehydrolysed kraft (R_{18} 98.4) and one Super I spruce sulphite pulp (R_{18} 94.5) with resin contents of 0.02 and 0.15 respectively.

Yarns of moderate strength were prepared in order to avoid the extreme sensitivity associated with high strength properties. One part of the sulphite pulp was extracted with acetone to remove the resin and this sample was incorporated in the spinning series. It is evident (*Figure 6*) that the resin has a noticeable influence on the stability of the strength upon heating. The changes in the elongation of the yarn also reflect the adverse influence of the

INFLUENCE OF PULP RESIN ON PROPERTIES OF HWM-FIBRES

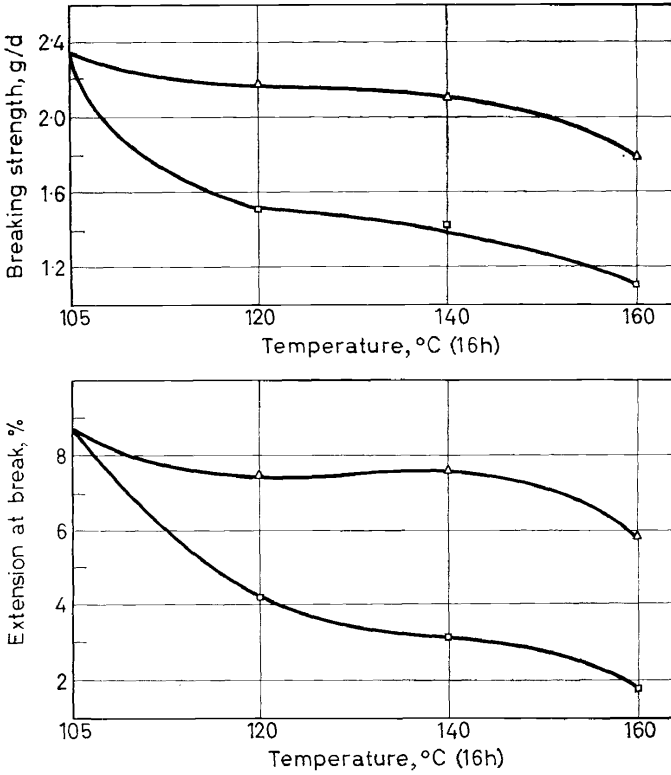


Figure 5. Heat stability of rayon produced from standard pulps [\triangle — \triangle , Resin in the pulp and silk 0.12 and 0.05 per cent; \square — \square , Resin in the pulp and silk 0.53 and 0.26 per cent respectively]

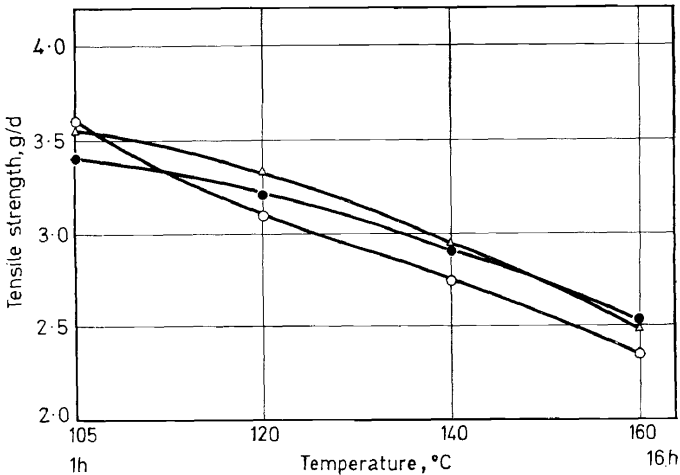


Figure 6. Tensile strength of HWM-fibres treated at different temperatures [\triangle — \triangle , Pre-hydrolysed sulphate, resin content 0.02 per cent; \bullet — \bullet , Super 1-sulphite, extracted; \circ — \circ , Super 1-sulphite, resin content, 0.15 per cent]

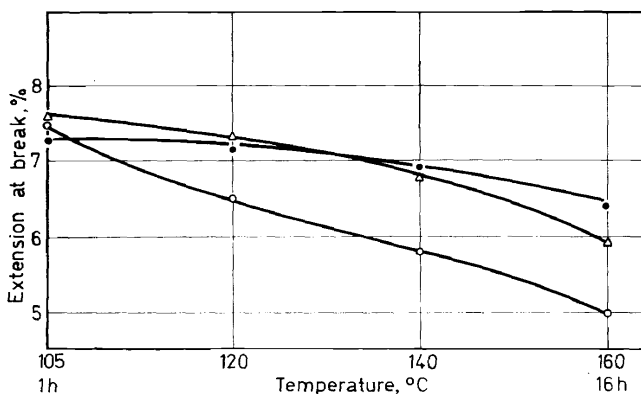


Figure 7. Extension of HWM-fibres treated at different temperatures [\triangle — \triangle , Pre-hydrolysed sulphate, resin content 0.02 per cent; \bullet — \bullet , Super 1-sulphite, extracted; \circ — \circ , Super 1-sulphite, resin content, 0.15 per cent]

resin (Figure 7) and although all resin contents are at a low level (less than 0.15 per cent), the pulps are clearly different.

An analysis of the change of the degree of polymerization during these treatments indicated that the resin influences reactions cleaving the polysaccharide chains during the heat treatment (Figure 8). Microscopic investigations have shown that transverse cracks in the thread are obtained by heating, i.e. local centres of degradation have been formed, where the cellulose chains certainly have a very low DP. It is possible that these flaws are initiated from resin particles. As mentioned earlier the resin in the fresh pulp has a chlorine content of about 15 per cent. Part of the chlorine is split off during production and storage of the pulp and part is split off

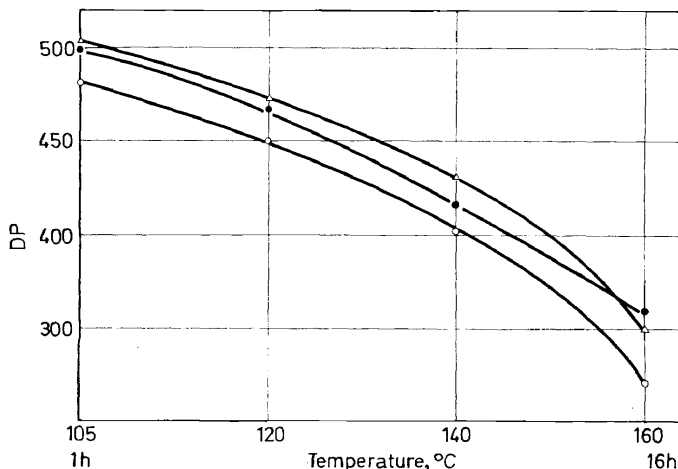


Figure 8. The change of the polymerization by heating HWM-fibres [\triangle — \triangle , Pre-hydrolysed sulphate, resin content 0.02 per cent; \bullet — \bullet , Super 1-sulphite, extracted; \circ — \circ , Super 1-sulphite, resin content 0.15 per cent]

INFLUENCE OF PULP RESIN ON PROPERTIES OF HWM-FIBRES

during the viscose making. Resin isolated from viscose, however, still contains about 10 per cent chlorine. It is well known that resin upon heating liberates acid gases (hydrochloric acid, formic acid, acetic acid, etc.). At least 3 per cent of the resin is liberated in the form of hydrochloric acid at 120°C. The same phenomenon is expected to occur when the yarn is heated, e.g. during drying, ironing or pressing of fabrics etc.

To prove that products split off from resin have a degrading effect on HWM-yarn we heated de-resined silk for 16 h at 120°C in a jar both with and without resin in the bottom. The silk was placed on a rack 5 cm above the bottom of the jar. There is no doubt that the resin has a very strong influence on the tensile strength, elongation and degree of polymerization of the silk after the treatment (*Table 1*). The replacement of oxygen with helium lessened the extent of degradation drastically. We do not understand this effect unless radical reactions are involved.

Table 1. Heating of wet HWM-fibres in a closed jar at 120°C for 48 hours

<i>Sample</i>	<i>Atmo- sphere</i>	<i>Pulp</i>	<i>Breaking strength (g/den.)</i>	<i>Ratio†</i>	<i>Extension at break (%)</i>	<i>Ratio†</i>	<i>DP</i>
1. Without resin	Air	Prehydrolysed sulphate	3.75	1.00	7.0	0.93	290
2. With resin (2%)	Air	Prehydrolysed sulphate	3.45	0.92	6.5	0.87	195
3. With resin (10%)	Air	Prehydrolysed sulphate	2.29	0.61	4.3	0.58	83
4. Without resin	Helium	Prehydrolysed sulphate	3.90	1.04	7.1	0.95	351
5. With resin (10%)	Helium	Prehydrolysed sulphate	3.67	0.98	6.6	0.88	262

† The ratio to conditioned rayon.

When the wet HWM-fibres were extracted before the heat treatment a stabilization against degradation was also obtained. We have performed many experiments on sulphite pulps which have been given reduced resin contents (~ 0.05 per cent) during the bleaching operation and these all support our opinion that resin has a significant influence on the heat stability of rayon products.

BRIGHTNESS

Strength and colour stability during the ageing of staple fibre and rayon yarn are important factors for ensuring good properties over a wide field. These factors will certainly be accentuated in the future especially for the new HWM-fibres, which will replace cotton in white materials for blouses and shirts and so on where good colour stability is essential. The increased use of rayon for products which are sterilized (sheets and pillow cases, compresses, sanitary towels, etc.) necessitates their being resistant to this treatment without any substantial effect on strength and appearance. During the heating of rayon yarn, coloured degradation products are formed, which reduce the brightness of the product. The pulp's contents of hemicellulose (especially xylan, rich in uronic acids) and metals are of great importance. Overoxidation during bleaching of the pulp is detrimental as it initiates carbonyl and carboxyl groups which are sensitive to heat. However, the

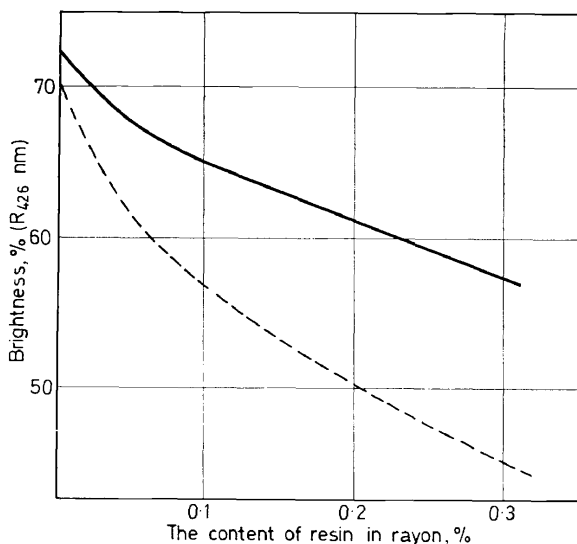


Figure 9. The brightness as a function of the resin content [(—), conditioned silk; (---), heated for 16 h at 120°C]

resin content of the pulp has in this case also, proved to be important. A high resin content gives a low brightness to the finished rayon product and its stability on heating becomes conspicuously lower (Figure 9).

In Figure 10 the brightness stability during heating of HWM-fibres from a Super 1-sulphite pulp before and after extraction and desulphurization is compared with that of fibres prepared from prehydrolysed kraft.

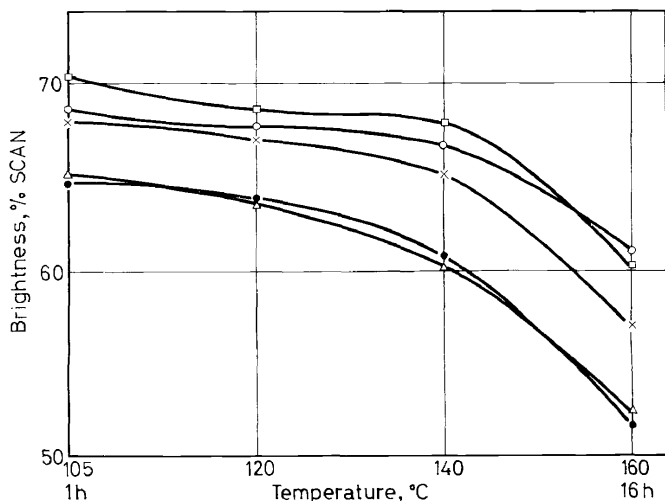


Figure 10. Brightness of HWM-fibres after different treatments [Super 1-sulphite: \triangle — \triangle untreated, \bullet — \bullet desulphurized, \circ — \circ extracted, \square — \square extracted and desulphurized; \times — \times pre-hydrolysed sulphate, untreated]

INFLUENCE OF PULP RESIN ON PROPERTIES OF HWM-FIBRES

The pulps are graded according to resin contents and the extracted Super I-sulphite pulp gives a yarn which is as stable as that from the prehydrolysed sulphate pulp, despite the fact that the degree of refinement of the sulphite pulp is about four R_{18} units lower.

The stability against ultraviolet light is of great importance to HWM-fibres as they are incorporated in fabrics which are used for outside wear. We have tested some of the yarn samples obtained in our investigation in a xenotester. The results are given in *Table 2*. It is evident from the figures in this table that the resin has an apparent influence on the u.v.-stability of HWM-fibre.

Table 2. Brightness reversion of HWM-fibres exposed to u.v. light

<i>Pulp</i>	<i>Resin content (%)</i>	<i>Brightness (% SCAN) before desulphurization</i>		<i>Brightness (% SCAN) after desulphurization</i>	
		<i>Conditioned</i>	<i>Aged</i>	<i>Conditioned</i>	<i>Aged</i>
		Super I-sulphite	0.15	61	52
Super I-sulphite extracted	0.01	64	62	66	66
Prehydrolysed kraft	0.02	65	60	69	66

As a consequence of the findings reported in this paper sulphite pulps, named Modocell LR and Modostar, have been developed. Some characteristics of Modostar, especially designed for the production of HWM-fibres

Table 3. Some properties of Modostar

R ₁₈ , Insoluble fraction in 18% NaOH	94.5%
R ₁₀ , Insoluble fraction in 10% NaOH	92%
Viscosity	50 cP
Ash	0.05%
Fe	5 p.p.m.
Dichloromethane extract	0.10%
Brightness	95%

are given in *Table 3*. The properties of the HWM-fibres from this pulp have fully come up to our expectations. It may be mentioned that in cooperation with our daughter company, Berol AB, a synthetic agent which improves filterability, but which does not have the detrimental effects of pulp resin, has been developed.

CONCLUSION

The influence of resin on the pulping and viscose processes has been the subject of extensive research in our laboratory over the last 3-4 years. It has been shown that resin adversely affects the viscose process and the finished rayon products. Although for some purposes the strength properties of HWM-fibres produced from low grade pulps with high resin contents may be acceptable, such important properties as stability of strength and colour

INGEMAR CROON, HEIMER JONSÉN and HANS-GUNNAR OLOFSSON

on ageing, heating and treatment with u.v. light are highly dependent on the amount of impurities present in the pulp. Among these impurities the resin is of vital importance.

The authors are indebted to Mo and Domsjö AB for the permission to publish this part of the investigation and to Professor O. Samuelson, Dr Treiber, Messrs U. Albertsson, A. Assarsson, B. Nelson, S. Regestad and T. Öhgren for valuable discussions.