VISCOSE-RAYON PULPS FROM CHILEAN HARDWOODS COIGUE, TEPA, AND ULMO

September 1951

No. R1906

UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison 5, Wisconsin
In Cooperation with the University of Wisconsin

VISCOSE-RAYON PULPS FROM CHILEAN HARDWOODS

COIGUE, TEPA, AND ULMO[1,2]

By

F. A. SIMMONDS,[3] Chemist
and
R. M. KINGSBURY, Chemist

Forest Products Laboratory,[4] Forest Service
U. S. Department of Agriculture

Abstract

A study was made of the possibility of producing pulp of viscose rayon grade from three Chilean hardwoods, coigue, tepa, and ulmo. Unbleached pulps were made from the three woods by (1) the neutral sulfite semichemical process with and without steam prehydrolysis, (2) a water prehydrolysis-sulfate process, and (3) the sulfite process. These pulps were purified by means of the conventional sequence of chlorination, alkaline extraction, oxidation, and acidic extraction. Yields of purified pulps, which contained from 2 to 7.5 percent of pentosans, ranged from 38 to 45 percent of the woods. Results of filtrability tests of viscose solutions from two of the pulps, of spinning trials on four of the pulps, and the general similarity of all of the pulps in chemical composition indicated that pulps acceptable for continuous-thread viscose rayon can be produced from the three woods by any of the processes investigated.

---

[1] To be presented at the 5th meeting of the Technical Committee on Wood Chemistry of the Food and Agriculture Organization of the United Nations, Appleton, Wis., September 17-18, 1951.

[2] In cooperation with the Chilean Development Corporation.

[3] Acknowledgment is made to the following members of the Forest Products Laboratory staff: J. N. McGovern, J. S. Martin, and E. L. Keller for the production of the unbleached pulps and constructive suggestions; to E. S. Lewis for assistance in the analytical and purification work; and to G. H. Chidester for his encouragement and guidance. Further acknowledgment is made to the Standards Department of the American Viscose Corporation where the spinning trials were held; to E. I. Du Pont De Nemours & Company, Inc., Rayon Dept., Technical Div., Viscose Research Laboratory, Richmond, Va., where the filtrability tests were made.

[4] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

Introduction

The Forest Products Laboratory, in cooperation with the Chilean Development Corporation, has investigated the possibility of producing pulps from three Chilean hardwoods, coigue (Nothofagus dombeyi), tepa (Laurelia serrata), and ulmo (Eucryphia cordifolia) that would be acceptable for continuous-thread textile rayon.

Analytical values typical of commercial pulps used for this grade of rayon were obtained from rayon producers. These values were:

Alpha cellulose	percent;	91.81
Beta cellulose	percent;	4.26
Gamma cellulose	percent;	4.33
Solubility in 7.14 percent sodium hydroxide solution	percent;	13.9
Dispersed viscosity (pulp at 0.5 percent concentration in cupri-ethylenediamine)	centipoises;	11.6
Ash	percent;	.09
Iron	parts per million;	10.
Copper	parts per million;	3.
Manganese	parts per million;	.5

Several pulping processes were applied to the three woods in order to determine the effect the pulping treatment had on the yield and quality of the purified pulp. All of the purified pulps were evaluated by conventional tests and, in certain instances, by filtrability tests of viscose solutions and by spinning trials.

Use of Hardwoods for Viscose Pulps

The problem of producing a pulp from which a commercial, filtrable, viscose solution can be made is common to all cellulosic source materials used for this purpose. As mentioned in a recent interpretive review on cellulose and wood pulp research (5),[5] the literature reveals much work directed toward identification of those characteristics of pulps which relate to unsatisfactory filtrability. These studies have dealt with the molecular properties of cellulose, the cell and so-called chemical composition of wood pulps, and the structure of the cells. The hypothesis that high-polymer fractions must be of abnormal composition (cross-bonded) to cause poor filtrability has also been proposed (1). Another hypothesis has been advanced concerning an interaction of hemicelluloses under the conditions of sulfate pulping. It is based on the assumption that upon the rupture of lignin-hemicellulose bonds, the released hemicelluloses cross-link and form stable anhydro hemicelluloses that may have an adverse effect on the filtrability of a viscose solution (14).

---

[5]Underlined numbers in parentheses refer to Literature Cited at end of report.

In another investigation, insoluble residues of viscose solutions were found to be higher in methoxyl content than the original pulps. This was interpreted as indicative of the presence of nonglucosidic groups in the cellulose chains (10). Another has concluded that the "resin" component of pulp has a direct and favorable effect on the xanthation reaction, and that consequently, if too little resin is present, poor filtrability will result (27).

Although a rational system for predicting the filtrability of viscose obtainable from a pulp has not appeared in the literature, an empirical staining technique using malachite green has been developed for this purpose (35). Its originator was able to classify pulps into five groups which would give viscose solutions ranging from nonfiltrable to readily filtrable.

The manufacture of viscose rayon from hardwood involves two problems peculiar to hardwoods. One is the high content of pentosan hemicellulose that must be removed; the other results from the short fibers and tracheids and the amount of parenchyma cells. Possibly neither of these is related to filtrability.

Because of the short fibers and tracheids and the high content of parenchyma cells, sheets of purified hardwood pulp are especially weak when in contact with a strong solution of sodium hydroxide. Difficulties encountered in industrial use because of this low strength include the breaking away of fibers from the sheets while they are steeping, the rupture of sheets while being pressed, and breakage of sheets as they are removed from the press.

The beating of purified pulp has been proposed as a means of increasing sheet strength sufficiently for conventional viscose preparation (22). The authors have been informed by a European manufacturer of hardwood viscose pulp that sufficient strength can be obtained by compressing the sheet in calendering to a density of approximately 1 gram per cubic centimeter. Slurry steeping, characteristic of the continuous process for preparing viscose, avoids the problem of low sheet strength. This technique was considered of considerable importance in the development of purified hardwood pulp in Germany (28), and its use has also been reported in the United States (4).

It has been concluded that the parenchyma fraction of European beech sulfite pulp of viscose grade (about 15 percent) has no harmful chemical effects (9). A screen fraction containing about 80 percent of parenchyma cells underwent xanthation more rapidly than did the remaining fraction of the pulp, which contained mostly fibers and tracheids. Any filtration difficulties were said to arise from the coarser of the two fractions. The finer fraction was about 4 percent lower in alpha cellulose, and its degree of polymerization was 520 as compared to 850 for the coarser fraction. This variation of cells in degree of polymerization was observed in the case of a bleached sulfate eucalyptus pulp (16).

The facts that in this country a purified hardwood sulfite pulp has been used for a number of years and that a purified hardwood sulfate pulp has come into use recently are sufficient evidence that this type of pulp is chemically suitable and can be adapted to the mechanical requirements of the viscose process.

The extensive literature on the removal of hemicelluloses by pulping and subsequent purification and the associated effects, especially with reference to pentosans, has been summarized comparatively recently (14, 15, 16, 17, 31) to provide a thorough correlative digest.

The desirability of a low proportion of pentosans in pulp for chemical conversion is widely emphasized. Hemicelluloses are converted to viscose as readily as is cellulose (5), and when converted are considered to have injurious effects on the properties of the regenerated fibers (3). Yet one "specification" would permit up to 4 percent of pentosans in viscose pulp, although with the qualifying recommendation that material with a degree of polymerization under 150 should be at a minimum (12).

It has been pointed out (29) that in the German staple-fiber industry it had been concluded from experiments that material of low degree of polymerization in pulps was harmful to the quality of the fiber, especially its strength when wet, and that material with a degree of polymerization of above 600 caused difficulties in operation associated with high solution viscosity. In a study (2) of the influence of polymolecularity of viscose rayons and of the corresponding cotton and wood pulps on certain mechanical properties of the rayons, a high degree of correlation was found between the amounts of material of low degree of polymerization in the pulps and corresponding rayons, somewhat less between the ratio of weight to average degree of polymerization of the rayons and tenacity, and a fair degree between the amount of material of low degree of polymerization in the rayons and resistance to fatigue. It was concluded that the ratio of weight to average degree of polymerization and the amount of material of low degree of polymerization influence fatigue resistance of rayon to about the same degree. It was further suggested as fairly probable that most of the material low in degree of polymerization is removed from the pulp during the conventional steeping treatment and that the material low in degree of polymerization is produced during aging of the alkali cellulose. If this is true, and from the correlations cited, it would follow that the amount of material of low degree polymerization should be kept as low as possible and that the duration of aging of the alkali cellulose should be as short as possible.

Chain-length distribution curves showing the changes occurring in the cellulose during the production of sulfite viscose pulp and tire cord from pine grown in the southern States, resulted in the theory that wood cellulose is comprised of only two fractions, namely, gamma (hemicelluloses), and alpha, and that the beta cellulose of a wood pulp is not a hemicellulose of wood, but rather a result of degradation of the alpha fraction during pulping and purification (18). Unpublished data of the present authors appear to support this theory. Conventional beta and gamma cellulose values were obtained for holocellulose isolated from southern pine wood and from southern pine pulp prepared by a prehydrolysis-sulfate process. The beta values, based on the wood, increased from 0.5 percent for the wood to about 2 percent for the purified pulp. The gamma values decreased from 19 percent for the wood to 0.9 percent for the purified pulp.

Available data indicate that beta cellulose and hemicelluloses are relatively low in molecular weight. The degree of polymerization values reported for beta cellulose range from 10 to 150 (11, 30). The fractions of European beech and spruce extracted in an 8 percent solution of sodium hydroxide and

then purified, were found to have degree of polymerization values of 150 and 160 (7). These purified fractions were considered to be xylan and mannan. A crystalline xylan from American paper birch had a degree of polymerization value of 35 (36).

It is of interest to summarize the values for southern pine sulfite pulp which have been reported for viscose rayon of tire cord grade. Proportions of alpha, beta, and gamma celluloses and pentosans were, respectively, 95.00, 2.50, and 1.98 percent (19). It appears from a chain-length distribution curve for this kind of pulp (18) that the fraction with a degree of polymerization value of 150 or less amounted to only about 4 percent, and the fraction with a value of 500 or less, about 7 percent. If this interpretation is correct, it appears that the gamma and pentosan values are actually related to the same fraction unless it is assumed that the pentosans were all in the alpha cellulose, which is doubtful for pulp made from softwood. It has been suggested that gamma cellulose is a mixture of pentosans and a constituent which absorbs chlorine (25).

When pulping is done under acidic conditions, the removal of hemicellulose is not generally a problem, even in the case of hardwoods (23), and it might also be inferred, from a lack of evidence to the contrary, that filtrability is not a problem. It is well known, however, that both the removal of hemicellulose and filtrability become problems when nearly neutral or definitely alkaline conditions are used for pulping. For an unbleached pulp having a high proportion of hemicelluloses the preferred hot alkaline process is not adequate, and the required cold process is not generally attractive economically. These two processes have been reviewed comprehensively in recent years (15, 16).

The possibility of producing viscose pulps by an alkaline pulping process has been studied because it is suitable for any kind of wood (8, 20). Prehydrolysis was developed as an adjunct for the removal of hemicelluloses (24, 26). A possibly unforeseen but important result of the prehydrolysis-alkaline pulping sequence (specifically, prehydrolysis-sulfate) is the high quality of viscose rayon obtainable from this kind of pulp (32). An additional benefit attributed to prehydrolysis is an improvement in the behavior ("reactivity") of sulfate pulp in conversion to viscose yarn (28, 34). Although a pine sulfate pulp, prepared by the cold alkaline extraction of bleached pulp, was used for a time in Germany for the production of viscose rayon tire cord, the prehydrolysis-sulfate type was preferred when it became available (6). The only information generally available on the commercial production and use of sulfate viscose pulps deals with German practice (6, 13, 28, 34).

By applying a prehydrolysis-sulfate process and a conventional 3-stage bleaching treatment to Australian eucalyptus, purified pulps were obtained which contained less than 2 percent of pentosans and up to 95.5 percent of alpha cellulose (17).

The possibilities of producing a viscose grade of pulp by acidic hydrolysis of sulfate pulp prepared from sugar maple have been investigated (31), but the process does not appear to be economically feasible. An acidic treatment of pulp that utilizes the acid formed in a chlorination stage, has been patented as a procedure in the purification of pulp for viscose (21). The preferred temperature is 40° C., and the maximum is 100° C. for a period of from 10 to 200 minutes. It is said

that this procedure removes pentosans, and that lowering of the viscosity can be controlled more closely and with less harm to the alpha fraction than when oxidation is used for this purpose.

The same principle is found in a patented procedure in the production of bamboo pulp, the treatment in this instance consists of heating for 1 hour in the temperature range of 90° to 150° C. and a pH of 2. The proportion of alpha cellulose was high in pulps made by this procedure (33).

Woods Used in the Present Study

Results of the tests applied to the samples of Chilean coigue, tepa, and ulmo used in the present study are given in table 1. These test methods, as well as those applied to the pulps, are identified in the Appendix.

The coigue and tepa were of medium density and in that respect were comparable to North American hardwoods, such as American elm, water tupelo, and sweetgum. The ulmo was much higher in density than the coigue and tepa, being comparable to the North American maples, birches, and some of the oaks.

In chemical composition, the three woods were typical of hardwoods in general. The alpha cellulose contents, however, were at the relatively high level of approximately 48 percent, and the pentosan contents of the tepa and ulmo were in the low range. Although the pentosan content of the tepa was only 13.7 percent, an earlier sample contained 17.7 percent pentosans. The amount of ether-extractable material in the three woods was in the low range for hardwoods, but the coigue contained twice as much as either the tepa or ulmo, a difference that was reflected in the purified pulps.

Preparation of the Unbleached Pulps

The processes used to make unbleached pulps from each of the three hardwoods were (1) neutral sulfite semichemical, with and without prehydrolysis, (2) prehydrolysis-sulfate, and (3) the acid sulfite. Stainless-steel, steam-jacketed, tumbling digesters were used. Pulping conditions are given in table 2.

Semichemical Pulping

Previous experience had indicated that the optimum lignin content for semichemical pulps to be bleached was about 10 percent. Thus conditions were established in the preliminary neutral sulfite semichemical digestions to produce semichemical pulps of approximately this lignin content both with and without a steam prehydrolysis of the chips. As previously mentioned, the purpose of the prehydrolysis step is to remove the hemicelluloses, which in hardwoods are chiefly pentosans.

The three woods responded differently to semichemical pulping. The ulmo was the most responsive, requiring the least chemical and shortest time. The coigue was somewhat less responsive, as shown by the higher chemical consumption and longer pulping time required. The tepa was considerably more resistant than the other two, and required a very large amount of chemical and, proportionately, a much longer equivalent cooking time. A digestion temperature of 180° C. was required in order to complete pulping in a reasonable time instead of the 170° C. needed for the others.

The steam prehydrolysis of the chips significantly decreased the time required for digestion but had essentially no effect on the amount of chemical required. It had, however, the effect of lowering the yield of unbleached pulp, due to the removal of hemicelluloses.

Only the prehydrolysis-semichemical pulp made from ulmo was purified because it was believed the results obtained on coigue and tepa afforded sufficient comparison between semichemical pulps made with and without prehydrolysis.

Sulfite Pulping

An ammonia-base sulfite liquor was used for pulping coigue and tepa because previous experience had shown those species to be incompletely pulped with conventional calcium-base liquor. Use of the ammonia-base was also expected to result in lower amounts of mineral matter and ether extractables in the pulps. Previous experience had also indicated that tepa is incompletely pulped with normal amounts of chemical, so a higher bisulfite content was used in the liquor for pulping that wood than for the coigue.

The coigue was pulped quite satisfactorily under the conditions used. A calcium-base sulfite liquor was found satisfactory for pulping ulmo under the conditions given in table 2.

Prehydrolysis-sulfate Pulping

The results indicate that the three hardwoods can be pulped readily with the prehydrolysis-sulfate process. Acids generated during prehydrolysis lowered the pH value to 4. Although the conventional sulfate process was not applied to the woods, it can be said from experience with other hardwoods and with Chilean insignis pine that the prehydrolysis step lowers the amount of chemicals required to produce pulps of approximately the same lignin contents. In addition, the combination of prehydrolysis and sulfate pulping removes the hemicelluloses of hardwoods to an extent which permits the use of the hot extraction process with its attendant low requirement of sodium hydroxide. The descending order of ease of pulping by the prehydrolysis-sulfate process appears to be ulmo, coigue, and tepa, which was essentially the order for the semichemical and sulfite processes.

Yield and Analytical Values for the Unbleached Pulps

The yield values for the unbleached pulps given in table 3 show that those for the semichemical pulps ranged from 54 to 67 percent and those for the chemical pulps from about 39 to 48 percent. A high yield is a characteristic of the conventional semichemical process, and the pulp obtained contains a considerable amount of lignin and hemicelluloses which have to be removed during the purification treatment.

With respect to yields of unbleached semichemical pulps made without prehydrolysis, the yield of tepa was very low in comparison with those for semichemical pulps of the same lignin content obtained from North American hardwoods, but the yields from coigue and ulmo were about the same. The yields of the unbleached pulps made with the prehydrolysis were lower than those of the corresponding pulps made without prehydrolysis, due to differences in the amounts of hemicellulose removed.

The alpha cellulose contents of the three hardwoods were all close to 48 percent (table 1). Losses of alpha cellulose in pulping can be determined by a comparison of that value with those for the unbleached pulps given in table 3. The comparison indicates that the semichemical process destroys less cellulose than the other two processes and that some destruction is to be expected by prehydrolysis. In general, the yields of alpha cellulose reported are considered to be good.

There was a tendency toward more destruction of cellulose by the prehydrolysis-sulfate process than by the sulfite process. The markedly higher viscosity values of the unbleached sulfate pulps accords with the relative severity of hydrolysis of the two processes. Although the high amount of lignin in the semichemical pulps prevented complete dispersion for the determination of viscosity, they may have been higher in degree of polymerization than any of the others because of the very mild pulping treatment. The chemical pulps differed in viscosity over a range of about 11 to 70 centipoises.

A comparison of the total pentosans present in the woods, and in the pulps made with the prehydrolysis step without added acid, shows that even very mild hydrolytic treatment is highly effective in the removal of pentosan hemicelluloses from hardwoods.

Owing to the generally small amount of pentosans removed in the subsequent purification of these pulps, it is likely that a greater degree of removal of pentosans in the pulping would have been advantageous to the quality of the purified pulps. More recent experience with aspen shows that a pentosan content as low as 3 percent in the unbleached pulp results from a slightly increased period of hydrolysis at maximum temperature.

A comparison of ether-solubility values suggests that prehydrolysis was advantageous in the removal of ether extractables.

It is of interest to compare the coigue prehydrolysis-sulfate pulp with the Australian eucalyptus (Eucalyptus regnans) previously referred to (34)

because of the similarity of the two raw materials and the differences in the pulping treatments. In the Australian work, the water prehydrolysis was done without added acid, as in the present study, but a higher temperature and a longer time were used. In the sulfate pulping, the maximum temperature was lower but a little more chemical and a longer time were used. For the eucalyptus pulp, the yield, alpha, and pentosan values were 32.5, 95.5, and 1.4 percent and, correspondingly, for the coigue pulp, 39.3, 94.3, and 7 percent. If one adjusts the yield value of the coigue pulp, in accordance with the lower pentosan content of the eucalyptus pulp and also allows for some additional loss, however, one may conclude reasonably that essentially the same character of viscose pulp and about the same yield is obtainable from Chilean coigue and Australian eucalyptus. On the same basis, it would be concluded that the yield of the very low pentosan type of pulp obtainable from the Chilean ulmo would be definitely higher than that from coigue.

Purification of the Unbleached Pulps

The conditions used for the purification of the unbleached pulps are given in table 4. A comparison of the total chlorine requirements of the pulps shows those of the semichemical pulps were much the highest, which accords with the high lignin contents of those pulps. Their chlorine requirements were in the range observed for neutral sulfite semichemical pulps of the same lignin contents made from North American hardwoods.

The high amount of hemicelluloses, chiefly pentosans in the semichemical pulps made without the prehydrolysis step, made it necessary to use the cold extraction process, following chlorination, in order to remove the required amount of hemicelluloses. For the coigue, the amount of alkali required in the cold extraction of the semichemical pulp was 13 times more than the amount required for the corresponding prehydrolysis-semichemical pulp, and similarly, for the tepa semichemical pulp, it was a little over three times. Although the hot alkaline extraction process was adequate for all of the other pulps, the tepa and ulmo semichemical pulps required from 2 to 3 times more alkali than did the others in this group which were quite similar in their requirements.

A final steeping in acidic solution was applied to the pulps as described in table 4 to lower iron content. These treatments had only a slight effect on dispersed viscosity. The iron was a result of contamination rather than from the woods from which the pulps were made.

As previously mentioned, the unbleached pulps differed a great deal in viscosity. Because of this, they were not processed to a common minimum viscosity. However, the decreases effected during purification ranged from 4 to 53 centipoises.

Yield and Test Values for the Purified Pulps

Yield and analytical values for the purified pulps are given in table 5.

Although the yields of the purified pulps are not directly comparable because of the differences in alpha and beta cellulose contents, it is believed even the lowest would compare favorably with the yields obtained in present commercial production. It is understood that the potential yield of viscose rayon yarn is sometimes estimated to be the sum of the amount alpha cellulose plus one-half the amount of beta cellulose in the pulp. The following tabulation arranges the pulps in descending order of yield on that basis:

Kind of pulp	Estimated yield of viscose rayon yarn Percent based on wood[6]
Coigue neutral sulfite semichemical	44
Coigue prehydrolysis-neutral sulfite semichemical	42
Coigue sulfite	42
Ulmo prehydrolysis-sulfate	41
Ulmo prehydrolysis-neutral sulfite semichemical	41
Tepa neutral sulfite semichemical	41
Tepa prehydrolysis-neutral sulfite semichemical	40
Ulmo sulfite	39
Tepa prehydrolysis-sulfate	39
Coigue prehydrolysis-sulfate	37
Tepa sulfite	36

The foregoing tabulation indicates that the highest yield of yarn from the three hardwoods can be obtained by means of the semichemical process, the next highest by the prehydrolysis-sulfate process, with the sulfite process third in order. The yield value given for the coigue prehydrolysis-sulfate pulp is believed to be somewhat low due to the conditions used in pulping and purification or to experimental error. The results also indicate that slightly higher yields may be expected from coigue and ulmo than from tepa.

In general, the chemical composition of the purified pulps met the requirements, which had been selected on the basis of analytical values typical of commercial sulfite viscose pulps, known to be acceptable for continuous-thread viscose rayon. The tepa sulfite pulp was definitely high in sodium hydroxide solubility and the ulmo prehydrolysis-semichemical and sulfite pulps were at the upper limit of acceptability in this respect.

There was indication of a trend toward higher disperse viscosity in the semichemical pulps than in the other two kinds. There was also a trend toward

---

[6] Values adjusted to nearest whole number. Order was not affected by so doing.

higher viscosity in the sulfite pulps than in prehydrolysis-sulfate pulps, if the greater degree of pulping used in the preparation of the tepa sulfite pulp is discounted.

With the exception of the tepa sulfite pulp, all of the experimental pulps were high in pentosans in comparison with values typical of commercial softwood sulfite viscose rayon pulps. Data obtained in the present study and earlier but unpublished data, indicate that in a softwood viscose pulp only a small proportion of the total pentosans are in the alpha cellulose, but that in a purified hardwood pulp, from 75 to 100 percent of the pentosans are in the alpha cellulose and, furthermore, they appear in the yarn. An analysis for pentosans made on yarn from the coigue semichemical pulp gave a value of 6.6 percent.

It would be desirable to have available a comparison of the properties of yarns and films made from a series of hardwood prehydrolysis-sulfate pulps varying as widely as feasible in pentosan content.

Despite the final steeping in acidic solution, the iron content of all of the purified pulps was very high. This indicates the residual iron was present as discrete particles. Since the experiments described here were made, a comprehensive survey of sources of contamination by iron in the small-scale and pilot plant bleaching operations has resulted in the practical elimination of this difficulty.

The pulps differed in viscosity over a range of about 6 to 23 centipoises.

Screen-fractionation data for three of the coigue pulps are given in table 6. These data show that about 60 percent by weight of coigue pulp was retained on an 80-mesh screen and about 20 percent passed through a 150-mesh screen under the conditions of fractionation used.

Strength of Sheets Wet with Sodium Hydroxide

As previously mentioned, the low strength of sheets of hardwood dissolving pulps when wet with a strong sodium hydroxide solution has been said to be a source of difficulty in the conventional process for the manufacture of viscose rayon.

It was reported that sheets of purified coigue sulfite pulp split to some extent during the steeping treatment in connection with viscose filtrability tests. No failures of any sort, however, were reported for the sheets of the purified tepa prehydrolysis-sulfate pulp. This suggests the possibility of adequate strength in the sulfate type of pulp.

Filtrability of Viscose Solutions from Experimental Pulps

The filtrability of viscose solutions made from the tepa-prehydrolysis-sulfate, the coigue sulfite, and certain commercial pulps was determined by an industrial viscose laboratory. In comparison with a European softwood sulfate pulp of viscose grade, the tepa sulfate pulp had the same dispersed viscosity, the alkali cellulose required less aging, the combined sulfur in the viscose was the same, the rate of ripening of the viscose was essentially the same, and the viscose was definitely superior in filtrability.

The coigue sulfite pulp had three times the dispersed viscosity of a sulfite viscose pulp, prepared commercially from a North American hardwood, and twice that of a similar softwood, but its reaction rate during aging was not significantly slower. The combined sulfur in the viscose from coigue pulp was about the same as that in the softwood control pulp, but less than that in the hardwood pulp. Its rate of ripening was similar to the softwood pulp but faster than that of the hardwood pulp, and its filtrability was almost

as good as that of the hardwood and definitely better than that of the softwood sulfites.

Spinning Trials

Viscose rayon yarn of continuous-thread grade was made by an industrial laboratory from 5-pound samples of the two coigue semichemical pulps and the coigue and ulmo prehydrolysis-sulfate pulps, which ranged from 3.6 to 7.4 percent in pentosans. It was reported that the experimental pulps reacted normally toward the viscose-making process and that the experimental yarns were of commercially acceptable quality.

Conclusion

The results of the filtrability tests, the spinning trials, and the general similarity in chemical composition of all of the experimental pulps warrant the conclusion that pulps, chemically satisfactory for continuous-thread rayon, can be made from Chilean coigue, tepa, and ulmo by, (1) the neutral sulfite semichemical process, with or without a prehydrolysis step, (2) the prehydrolysis-sulfate process, and (3) the sulfite process in conjunction with suitable but simple purification treatments. The study also indicates that pentosans closely associated with the alpha cellulose of hardwoods may be less harmful to the quality of viscose products than the pentosans of softwoods.

Appendix

The standards used in evaluating the wood and pulps, listed in table 7, are those of the Technical Association of the Pulp and Paper Industry.

The solubility of the purified pulps in sodium hydroxide solution was determined according to Joint Army-Navy (U.S.) Specification, JAN-C-216, Cellulose, Wood Pulp. May 29, 1945.

Alpha, beta, and gamma celluloses were determined by the gravimetric procedure given in Forest Products Laboratory Report No. R19.

Amounts of iron and copper were measured according to Forest Products Laboratory spectrophotometric procedures. In either instance a pulp sample is put into solution by the oxidizing action of nitric, sulfuric, and perchloric acids. Orthophenanthroline is used to form the colored complex with iron and tetraethylene pentamine, with copper.

Literature Cited

(1) Centola, G.
1949. The Suitability of Cellulose Pulps for Rayon Production. Food and Agriculture Organization of the United Nations, 4th Meeting of the Technical Committee on Wood Chemistry 139-145, Brussels, August.

(2) Davis, W. E.
1951. Polymolecularity of Viscose Rayon and Rayon-grade Pulps. Ind. Eng. Chem. 43(2) 516-21, February.

(3) Dörr, R. E.
1942. The Problem of Cellulose and Cellulose Yarn. Kunstseide U. Zellwolle 22, 278-85 (1940); Chimie & Industrie 47, 239.

(4) Frisk, Paul Warner
1946. Importance of Adequate Steeping of Alkali Cellulose. Rayon Textile No. 27(12) 641-42, December.

(5) Heuser, Emil
1950. Trends in Fundamental Research in the Cellulose and Wood Pulp Field. Paper Mill News 73(37) 30-32, 34, 36, 90. September 16.

(6) Hill, Allan C., and Campbell, W. Boyd
Zellstoffabrik Waldhof. PB Report 7918. Office of the Publication Board, Department of Commerce, Washington, D. C., USA.

(7) Husemann, E.
1940. Constitution of Wood Polyoses. J. prakt. Chem. 155(1-5), 13-64, February 20.

(8) Kienitz, G. A.
1937. Beech Pulp by Alkaline Cooking Process. Holz Roh-u. Werkstoff 1 (1-2) 30-5, October-November.

(9) Klauditz, W., and Stegmann, G.
1944. Morphologically Conditioned Reactivity Differences on Xanthation of Fractions of Commercial Beech Sulfite Pulps. Cellulosechemie 22, 20-27.

(10) Kleinert, T., Hingst, G., and Simmler, I.
1944. Influence of Properties on Behavior in the Viscose Process. Kolloid-Z. 108, 137-44.

(11) Kraemer, Elmer O.
1938. Molecular Weights of Cellulose and Cellulose Derivatives. Ind. Eng. Chem. 30(10) 1200-03, October.

(12) Lindpainter, E.
1942. The Significance of Pentosans in Rayon Pulp and Their Removal by Alkaline Purification. Melliand Textilber. 23(6) 229-30, June. Svensk Papperstidn. 45(15) 309, August 15.

(13) McGovern, J. N.
1946. Manufacture of High Alpha Pulps in Wartime Germany. The Paper Ind. & Paper World, 28, 988-90, October.

(14) McKinney, J. W.
1946. The Effect of Alkaline Pulping on the Acetylating Properties of Wood Pulp. Paper Trade Jour. 122(4) 58-62, January 24.

(15) Meller, Alexander
1946. The Hot Alkaline Purification of Cellulose I. Paper Trade Jour. 121(13) 133-45, September 27, 1945; II. Cooking of Pine Wood by the Sulfate Process in One and Two Stages and the Hot Alkaline Purification of Pine Sulfate Pulp. Paper Trade Jour. 123(26) 49-54, December 26.

(16) _____
1947. The Cold Alkaline Purification of Wood Cellulose I. Some Effects of Bleaching and Acid Hydrolysis on Resistant Pentosans. Paper Trade Jour. 124(9), 57-60, February 27; II. Influence of Surface Properties on Resistant Pentosans. Paper Trade Jour. 125(11), 57-60, September 11.

(17) _____
1950. Eucalypt Pulps from Water Prehydrolysis and Sulfate Pulping. Tappi 33(5) 248-53, May.

(18) Mitchell, R. L.
1946. Chain Length Measurements on Nitrated Cellulosic Constituents of Wood. Ind. Eng. Chem. 38(8) 843-50, August.

(19) _____
1949. Viscose Processing of Cellulose. Changes in Basic Properties. Ind. Eng. Chem. 41(10) 2197-2201, October.

(20) Nickel, S.
1938. The Chemical Conversion of Pulps Made by Alkaline Pulping. 1. Viscose Staple Fiber from Pulps made by Alkaline Pulping. Holz Roh-u. Werkstoff 1(10) 388-90, July.

(21) Norta, Turma, and Sivola, Yrjo
1948. Process of Making and Refinishing Chemical Pulp. Canadian Patent 461,267, November 22, 1949; Swedish Patent 122,741, September 14.

(22) Richter, G. A.
1930. U. S. Patent 1,754,437, April 15,

(23) _____
1941. Cellulose from Hardwoods. Ind. Eng.Chem. 33(12) 1518-28, December.

(24) _____
1931. U. S. Patents 1,787,953, January 6; 1,819,002, August 18.

(25) Ritman, E. L.
1933. The Real Meaning of Beta and Gamma Cellulose. World's Paper Trade Rev. 100, 968-74.

(26) Rosa, Sr., de la, Joaquin Julio
U. S. Patents 1,782,869, November 25, 1930; 1,864,985, June 28, 1932.

(27) Samuelson, Olof
1949. Investigations Concerning the Filtering Properties of Viscose. III. Svensk Kemisk Tidskrift. 61, 227-34.

(28) Smith, Leroy H.
1946. Synthetic Fiber Developments in Germany. P. 14 Textile Research Institute, Inc., New York.

(29) Spurlin, H. M.
1943. Influence of Polymolecularity on Physical Properties. Cellulose and Cellulose Derivatives, Emil Ott, Editor, New York.

(30) Staudinger, H., and Jurisch, I.
1939. Macromolecular Compounds. Kunstseide U. Zellwolle 21, 6-9.

(31) Tasker, C. W., and Libby, C. E.
1946. The Manufacture of Viscose from Sugar Maple. Paper Trade Jour. 123(24) 139-48, December 5.

(32) Tippets, E. A.
1950. The Position of Cellulose as a Chemical Raw Material. Tappi 33(2), 32A, 34A, February.

(33) Trivedi, S. A.
1950. Indian Patent 42,068, December 6.

(34) Wicker, Don B.
1945. Sulfate Dissolving Pulp for Rayon Manufacture. P. B. Report 1130, Office of the Publication Board, Department of Commerce, Washington D. C., USA, September 19.

(35) Winkler, Werner
1950. Determining the Suitability of Dissolving Pulps for Viscose Manufacture. Kunstseide U. Zellwolle 28(5), 153-55.

(36) Yundt, Albert P.
1951. Crystalline Hemicelluloses. Tappi 34(2) 89-95, February.

Table 1.--Physical characteristics and chemical constituents of the Chilean hardwoods, coigue, tepa, and ulmo

Determination	Kind of wood		
	Coigue (Nothofagus dombeyi)	Tepa (Laurelia serrata)	Ulmo (Eucryphia cordifolia)
Physical characteristics:[1]			
Specific gravity[2]	0.465	0.418	0.548
Density[2], lb. per cu. ft.	29.0	26.1	34.2
Proportion of incipient decay to total wood, percent	3.65	10.83	2.24
Proportion of advanced decay to total wood, percent	3.59	0.0	.11
Average diameter inside of bark, inches	20.3	20.8	22.0
Average age, years	117	225	243
Average rate of growth, rings per inch	11.5	21.6	22.1
Chemical constituents:[3]			
Lignin, percent	23.2	28.2	26.2
Holocellulose, percent	70.4	71.3	76.5
Alpha cellulose[4], percent	47.6	48.0	48.6
Pentosans, total present, percent	17.3	13.7	14.9
Ash, percent	.3	.8	.5
Alcohol-benzene extractables, percent	6.1	1.4	1.8
Ethyl ether extractables, percent	.6	.3	.3
Hot water extractables, percent	6.6	2.1	3.4
Sodium hydroxide[2] extractables, percent	18.2	9.7	16.5

[1] Average values obtained on transverse sections of all logs used in the experiments.

[2] Calculated on the basis of weight of moisture-free wood and volume of green wood.

[3] Determined on representative samples of chips used in pulping experiments.

[4] Determined on holocellulose.

[5] The concentration of sodium hydroxide in water solution was 1 percent by weight.

Table 2.--Conditions used in preparing unbleached pulps from coigue, teca, and ulmo

Wood	Coigue				Teca				Ulmo			
Process	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]		Sulfate	Sulfite
	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Calcium base
Digestion No.	5238N	5266N	2953	5236I	5265N	5297N	2951	5237I	542Y	621Y	2950	5300I
Pretreatment:												
Maximum pressure, p.s.i.	(2)	[3]110			(2)	[3]110			(2)	[3]110		
Maximum temperature, °C.	(2)		[4]160		(2)		[4]170		(2)		[4]170	
Elapsed time to maximum temperature, hr.:min.		0:45	1:15			0:45	1:30			0:45	1:30	
Elapsed time at maximum temperature, hr.:min.	0:35	0:15	0:0		0:30	0:15	0:0		0:30	0:15	0:0	
Total elapsed time, hr.:min.	0:35	1:00	1:15		0:30	1:00	1:30		0:30	1:00	1:30	
Acidity at end, pH			3.97				4.19				3.97	
Digestion:												
Chemicals:[5]												
Sodium sulfite, percent	20.5	18.9			38.0	37.6			15.6	16.1		
Sodium bicarbonate, percent	11.0	7.4			15.4	15.8			6.4	7.0		
Sodium hydroxide, percent			14.1				15.5				14.1	
Sodium sulfide, percent			5.9				6.5				5.9	
Sulfur dioxide:												
Combined, gm. per 100 ml.				1.10				1.44				1.19
Total, gm. per 100 ml.				5.88				6.00				6.02
Maximum temperature, °C.	170	170	170	140	180	170	170	140	170	171	170	140.
Elapsed time to maximum temperature, hr.:min.	0:10	0:15	1:30	4:30	0:30	0:25	1:30	4:30	0:10	0:05	1:30	4:30
Elapsed time at maximum temperature, hr.:min.	2:45	0:45	1:0	2:15	3:30	5:0	1:30	8:45	1:30	0:40	1:0	5:30
Total elapsed time[6], hr.:min.	2:55	1:0	2:30	6:45	4:0	5:25	3:0	13:15	1:40	0:45	2:30	10:00

[1] Neutral sulfite semichemical. The partially digested chips were separated into a fibrous condition by means of the disk-attrition type of mill. After being screened, these pulps ranged in freeness from 600 to 770 ml., Schopper - Riegler.

[2] Preteamed at atmospheric pressure.

[3] Steam hydrolysis

[4] Water hydrolysis.

[5] Percentage values based on wood.

[6] For N.S.S.C. pulps, values do not include one hour used for impregnation of chips with cooking liquor at 120° C., following which the excess liquor was drained from the digester before cooking at a higher temperature.

Table 3.--Yield and analytical values for unbleached pulps made from coigüe, tepa, and ulmo

Wood	Coigüe				Tepa				Ulmo			
Kind of pulp	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]		Sulfate	Sulfite
	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	Without prehydrolysis	With prehydrolysis	Prehydrolysis (2)	Calcium base
Digestion No.	5238N	5266N	2953	5236I	5265N	5297N	2951	5237I	542Y	621Y	2950	5300I
Yield, percent	66.6	50.4	39.3	47.0	54.4	54.4	42.0	41.2	71.2	58.3	43.4	43.5
Permanganate No.	38.0			15.8			11.3	4.0			9.6	8.4
Lignin, percent	9.8	10.1	2.1	1.8	10.3	11.4	2.8	1.1	11.0	12.5	1.5	2.3
Total cellulose, percent	82.3	87.9	98.0	96.6	83.7	84.6	97.0	99.0	79.2	84.0	94.7	98.1
Alpha cellulose:												
Basis pulp, percent	66.5	83.9	91.4	88.4	72.7	74.2	87.0	92.2	64.6	74.3	93.1	88.3
Basis wood[3], percent	44.4	42.3	35.9	41.5	39.5	40.4	36.4	38.0	46.1	43.3	40.4	38.4
Total pentosans, percent	19.1	5.0	7.0	6.7	10.6	5.5	6.7	3.7	15.2	8.7	4.3	4.5
Solubility in ether, percent	1.2	.55	.3	.6	.4	.15	.4	.2	.2	.2	.7	.6
Viscosity[4], cp.			70.1	35.4			16.1	10.7			53.7	20.5
Ash, percent	1.4	.8	.4	.4	1.0	1.2	1.2	.3	1.1	.8	.4	.6
Brightness	31.7	20.2	30.2	42.2	30.1	27.6	30.3	48.0		18.7	25.2	32.0

[1] Neutral sulfite semichemical.

[2] Yield following prehydrolysis was 81.5 percent and pentosan content was 9 percent.

[3] The alpha cellulose contents of the three woods were approximately 48 percent.

[4] Pulp at 0.5 percent concentration in cupriethylenediamine.

ZM 80286 F

Table 4.--Conditions used in the purification of pulps made from coigue, tepa, and ulmo[1]

Kind of wood	Kind of pulp	Digestion No.	Purification No.	Stage 1	Stage 2			Stage 3[2]		
					Alkaline extraction			Oxidation		
				Chlorination	Sodium hydroxide	Temperature	Elapsed time	Chlorine as sodium hypochlorite	Temperature	Elapsed time
				Chlorine						
				Percent	Percent	°C.	Hour	Percent	°C.	Hours
Coigue	N.S.S.C.[3]	5238N	1268	15.0	47.0	25	1.0	1.0	30	5
	Prehydrolysis-N.S.S.C.	5266N	1331	12.0	3.6	80	.75	1.0	32	4
	Prehydrolysis-sulfate	2953	1340	2.0	3.0	80	.75	1.5	38	4
	Sulfite	5236I	1368	4.0	3.0	80	.75	1.0	30	5
Tepa	N.S.S.C.[3]	5265N	1493	15.0	32.3	24	1.0	.8	30	4
	Prehydrolysis-N.S.S.C.	5297N	1492	16.0	10.0	110	.75	1.0	32	4
	Prehydrolysis-sulfate	2951	1370	2.7	3.0	80	1.0	1.5	38	5.25
	Sulfite	5237I	1319	1.5	5.0	90	1.0	.5	30	4
Ulmo	Prehydrolysis-N.S.S.C.[3]	621Y	1518	18.0	10.0	91	.75	1.0	33	5
	Prehydrolysis-sulfate	2950	1333	2.0	3.0	81	.75	1.5	39	5
	Sulfite	5300I	1499	2.5	3.0	80	.75	.8	30	4

[1]Percentage values for chemicals used are based on weight of unbleached pulp. Consistence or density values in percent were: 2 for chlorination, 10 for alkaline extraction and oxidation, and 4 for acid extraction. Temperature during chlorination was 25° C. During oxidation with sodium hypochlorite, the pH was maintained at 8.5 to 9.

[2]Stage 4 was an acid extraction treatment. The treatment applied in Purifications Nos. 1268 and 1331 comprised first a steep in hydrochloric acid solution at pH 2 and a temperature of 25° C. for 1 hour, then a thorough washing and then a steep in hydrofluoric acid solution at pH 1.2 and 25° C. for 1 hour. The pulp was then washed, neutralized with ammonium hydroxide and washed again, all with solids-free water. The acid extraction treatment used for all other pulps comprised a steep in 1 percent oxalic acid solution at 25° C. for 1 hour.

[3]Neutral sulfite semichemical.

Table 5.--Yield and analytical values for the purified pulps made from coigue, tepa, and ulmo

Wood	Coigüe				Tepa				Ulmo		
Kind of pulp	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]		Sulfate	Sulfite	N.S.S.C.[1]	Sulfate	Sulfite
	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	Without prehydrolysis	With prehydrolysis	Prehydrolysis	Ammonia base	With prehydrolysis	Prehydrolysis	Calcium base
Digestion No.	5238N	5266N	2953	5236I	5265N	5297N	2951	5237I	621Y	2950	5300I
Purification No.	1268	1331	1340	1368	1493	1492	1370	1319	1518	1333	1499
Yield:											
Basis pulp, percent	68.2	86.7	97.6	93.4	79.8	79.6	97.0	90.7	75.2	94.6	94.7
Basis wood, percent	45.5	43.6	38.4	43.9	43.4	43.3	40.5	37.4	43.8	41.1	41.2
Alpha cellulose:											
Basis pulp, percent	[2]94.7	94.6	94.3	92.5	92.7	91.7	92.5	92.3	92.7	96.3	92.5
Basis wood, percent	43.0	41.4	36.2	40.6	40.2	39.7	37.5	34.3	40.7	39.6	38.2
Beta cellulose, percent	4.1	3.3	5.8	5.3	4.0	2.5	6.5	7.0	4.7	3.8	3.7
Gamma cellulose, percent	1.2	2.1	.0	2.2	3.1	5.7	1.0	.7	2.3	.0	3.7
Pentosans, percent	[2]7.4	3.6	6.7	4.5	7.3	6.3	5.6	2.1	8.9	4.4	3.6
Solubility in:											
Ether, percent	.25	.4	.3	.4	.1	.15	.0	.1	.2	.2	.2
Sodium hydroxide, percent	8.6	9.7	11.4	9.2	13.2	10.2	10.3	16.8	14.9	8.8	15.5
Viscosity[4], cp.	15.9	17.2	12.2	21.0	9.9	13.4	6.3	6.7	22.8	6.6	14.9
Ash, percent	.07	.07	.08	.11	.26	.14	.2	.13	.09	.07	.13
Iron, p.p.m.	[3]27.0	61.0	33.0	29.0	.....	46.0	33.0	20.0	.....	33.0	.....
Brightness	87.0	84.3	82.4	82.1	86.0	85.6	81.0	85.0	86.6	82.6	84.6

[1] Neutral sulfite semichemical.

[2] The alpha cellulose contained 8.2 percent pentosans which is equivalent to 7.7 percent based on the purified pulp. The rayon yarn made from the pulp contained 6.6 percent pentosans.

[3] The unbleached pulp contained 110 p.p.m. of iron.

[4] Pulp at 0.5 percent concentration in cupriethylenediamine.

Table 6.--Screen-fractionation data for unbleached and purified pulps from coigue

Pulp	Purification number	Fractions and amounts				
		Retained on 80-mesh screen	Retained between 80- and 115-mesh screens	Retained between 115- and 150-mesh screens	Retained between 150- and 200-mesh screens	Passing a 200-mesh screen by difference
		Percent	Percent	Percent	Percent	Percent
Neutral sulfite semichemical Digestion 5238N:						
Unbleached		67.2	9.8	3.5	1.5	18.0
Purified	1,268	66.7	14.5	4.9	2.0	11.9
Prehydrolysis-neutral sulfite semichemical, Digestion 5266N:						
Unbleached		56.6	16.9	4.2	.6	21.7
Purified	1,331	64.4	16.1	3.1	1.6	14.8
Sulfite, Digestion 5236I:						
Unbleached		60.6	17.6	3.5	2.7	15.6
Purified	1,368	50.8	21.0	3.1	3.3	21.8

Table 7.—TAPPI Standards[1] used in the evaluation of Chilean woods and the pulps made from them

Determination	Method number
Wood	
Specific gravity, density	T 18 m-47
Lignin	T 13 m-45
Holocellulose	T 9 m-45
Total pentosans	T 223 m-43
Ash	T 15 m-45
Solubilities:	
Hot water	T 1 m-45
One percent sodium hydroxide	T 4 m-44
Ether	T 5 m-45
Alcohol-benzene	T 6 m-45
Pulp	
Permanganate number	T 214 m-42
Lignin	T 222 m-43
Total pentosans	T 223 m-43
Ash	T 211 m-44
Ether solubility	T 5 m-45
Dispersed (solution) viscosity	T 230 sm-46
Brightness	T 217 m-47

[1] Technical Association of the Pulp and Paper Industry, 122 E. 42nd St., New York 17, N. Y.