M.ENG. MECHANICAL ENGINEERING

DYNAMIC MECHANICAL PROPERTIES OF THERMALLY AND CHEMICALLY TREATED SPRUCE AND BIRCH WOODS

M.I. Stationwala

ABSTRACT

Dynamic mechanical properties of dry and swollen, spruce and birch were studied in a torsion pendulum through the temperature range 20-240°C. The effect of pre-steaming at 180°C for 3 min. and of progressive delignification on these properties was also studied.

Elastic shear modulus decreased almost linearly but mechanical damping showed little change for dry spruce and birch, up to 220°C. Both species exhibited increased damping and a decrease in modulus when swollen with water. These changes became more pronounced with increase in temperature.

A well defined major second-order transition was observed at approximately 130°C for both untreated and pre-steamed specimens of spruce and birch swollen in glycerol. Glycerol has a similar though smaller plasticizing effect on both woods when compared to water. Delignification softens the wood and is accompanied by increased damping and a decrease of shear modulus; the transition temperature is lowered by an amount proportional to the lignin removed.

The implications of these results to the mechanical pulping of wood is discussed.

STATIONWALA DYNAMIC MECHANICAL PROPERTIES OF TREATED WOODS

DYNAMIC MECHANICAL PROPERTIES OF THERMALLY AND CHEMICALLY TREATED SPRUCE AND BIRCH WOODS

by

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A Thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of
the requirements for the degree of
Master of Engineering

Department of Mechanical Engineering
McGill University
Montreal

March 1969

ABSTRACT

Elastic shear modulus parallel to the grain and the mechanical damping of low frequency free torsional oscillations were measured for black spruce and white birch. Variation of these properties with temperature in the dry and swollen states was investigated through the range 20-240°C. The effect of presteaming at 180°C for 3 minutes and of progressive delignification with sodium chlorite were also studied.

There was a small, almost linear decrease in the elastic shear modulus but very little change in the mechanical damping of dry spruce and birch up to 220°C. Water-swollen spruce and birch exhibited higher damping and a much larger rate of decrease of shear modulus with temperature up to 100°C at atmospheric pressure.

A well defined second-order transition was observed at approximately 130°C for both untreated and presteamed specimens of spruce and birch swollen in glycerol. Glycerol has a similar though smaller plasticising effect on both woods when compared to water. Delignification softens the wood and is accompanied by increased damping and a decrease of shear modulus; the transition temperature is lowered by an amount proportional to the lignin removed.

The implications of these results to the mechanical pulping of wood is discussed.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to:

Dr. D. Atack for suggesting the problem and for his guidance, constructive criticism and helpful discussions throughout the investigation;

Mr. L.J. Vrooman for his help on electronic problems;

Mr. L.R. Heffell for procuring the wood samples and general assistance in setting up the equipment;

Mr. M. Murphy for preparing the drawings and graphs;

Dr. J.A.N. Scott for conducting UV microscope analyses on some delignified samples;

National Research Council of Canada for financial assistance during 1968-69;

and the Pulp and Paper Research Institute of Canada for a fellowship (1966-68) and liberal and generous use of their facilities and services.

TABLE OF CONTENTS

RESULTS

Dynamic Mechanical Properties of Spruce and Birch

Table of Contents (cont'd)

LIST OF FIGURES

List of Figures (cont'd)

FIGURE page

INTRODUCTION

The main objective of this study is to determine the effect of temperature on selected dynamic mechanical properties of spruce and birch. Such knowledge will assist in the development of new methods for processing these woods by thermomechanical means to produce paper-making pulps.

Many of the studies reported on the mechanical properties of wood have dealt with the measurement of, and the interrelation between, the elastic constants of air-dry samples of various species at room temperature. An excellent, comprehensive review of these studies has been given by Hearmon (1). Such data have been used extensively by engineering designers to predict the behaviour of wooden structures, appreciating the fact that individual components of any structure should not be subjected to stresses in excess of their elastic limit.

The mathematical theory of wood elasticity is based on the assumption that wood is a homogeneous anisotropic continuum possessing three mutually perpendicular planes of elastic symmetry. Anisotropy arises as a direct consequence of the wood structure. Thus, for instance, softwoods such as spruce are composed largely of tracheids whose morphology is shown schematically in Fig. 1 (2). A spruce tracheid is about 3 mm long and its polygonal, generally square, sides have a dimension of approximately 0.03 mm; the tracheid is hollow and

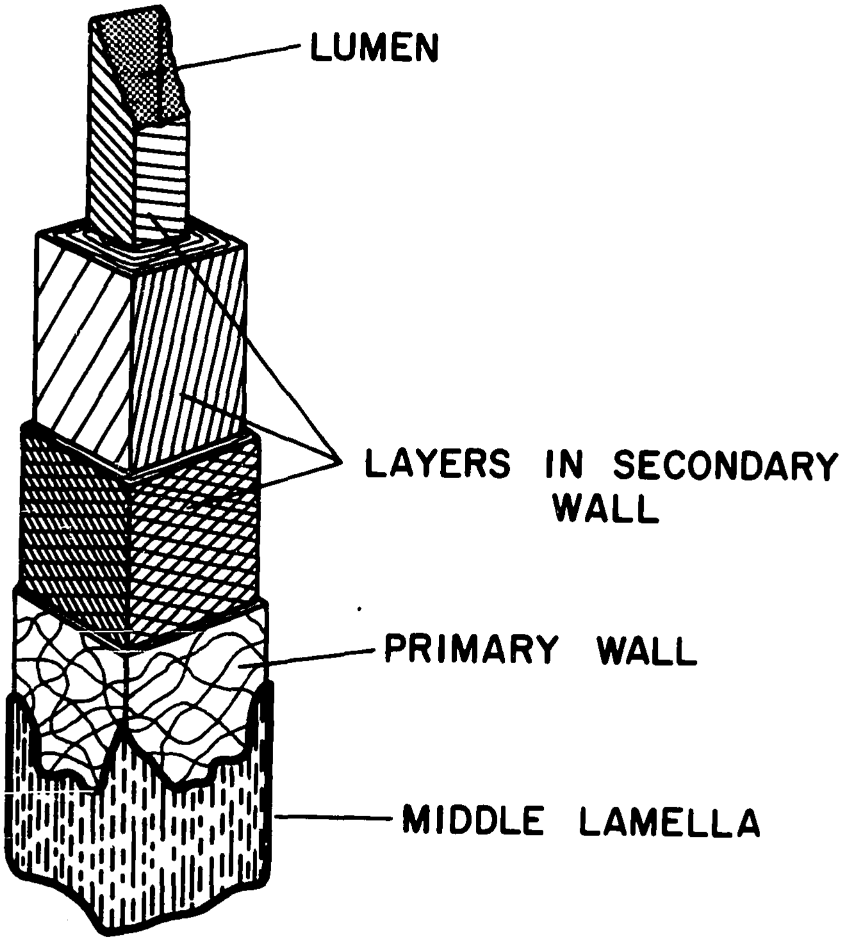


FIG. 1

Schematic representation of a softwood tracheid (2). The thin primary wall is highly lignified as is the surrounding middle lamella. Most of the cellulose and hemicellulose is in the secondary wall. The three layers of the secondary wall can be identified by the different orientation of their cellulose microfibrils.

and its walls are composed of several concentric lamellae of different physical structure and chemical composition. The longitudinal, L, axis of a tracheid is parallel to the vertical axis of the tree; adjacent edges of the cross section of a square tracheid are parallel to the radial, R, and tangential, T, directions in the cross section of a circular tree trunk. Fig. 2 is a composite photograph due to Koran (3) showing a typical small volume element of a spruce tree. Tracheids are seen to be bonded together along their radial and tangential faces and their longitudinal axes are parallel to the grain.

As expected, such a structure exhibits elastic moduli in the L-T and L-R planes which are quite similar and significantly different from the corresponding moduli in the R-T plane. Hearmon's classical contribution to the theory of anisotropic elasticity (4) has to some extent been based on an analysis of experimental data on wood in terms of the above model.

The use of wood for strong, light structures has been considerably extended by the development of laminated woods, plywoods and impregnated woods. These materials are more nearly isotropic than the parent wood from which they are made. A great impetus to the study of the mechanical properties of laminated woods arose from their extensive use in airframes during World War II. This use culminated in the production of the "Mosquito" fighter-bomber most of which

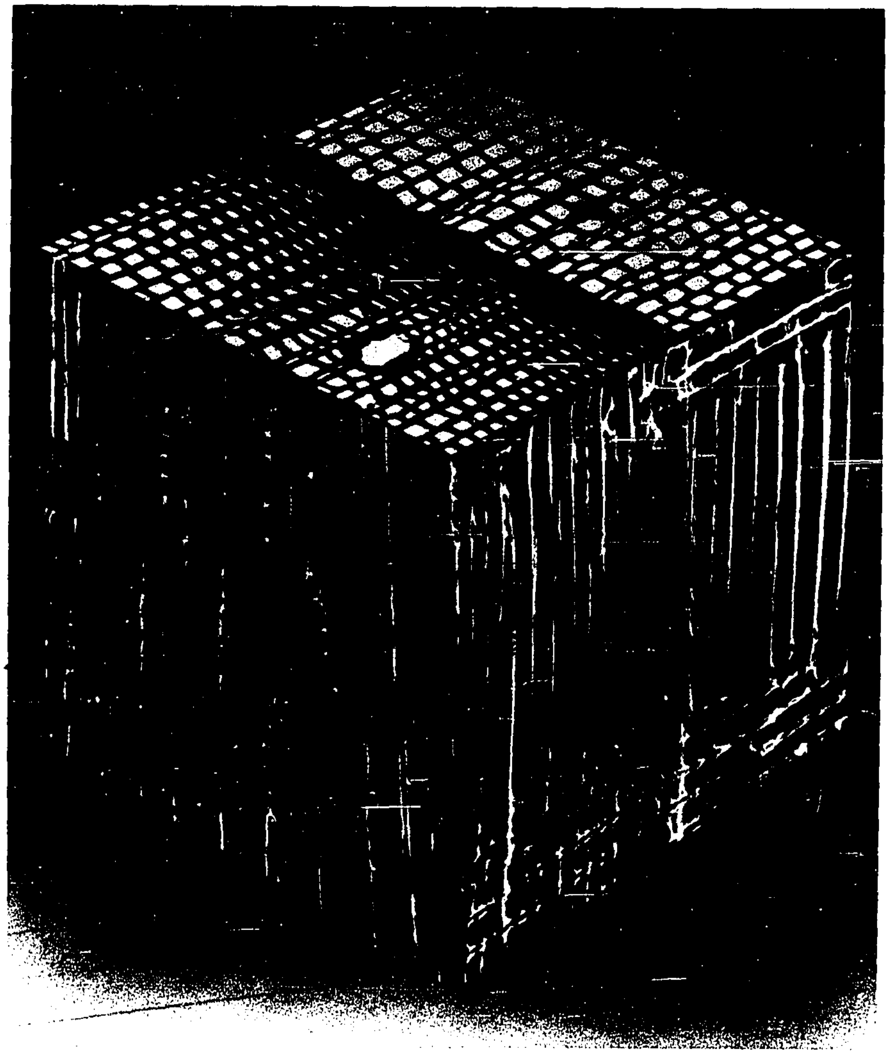
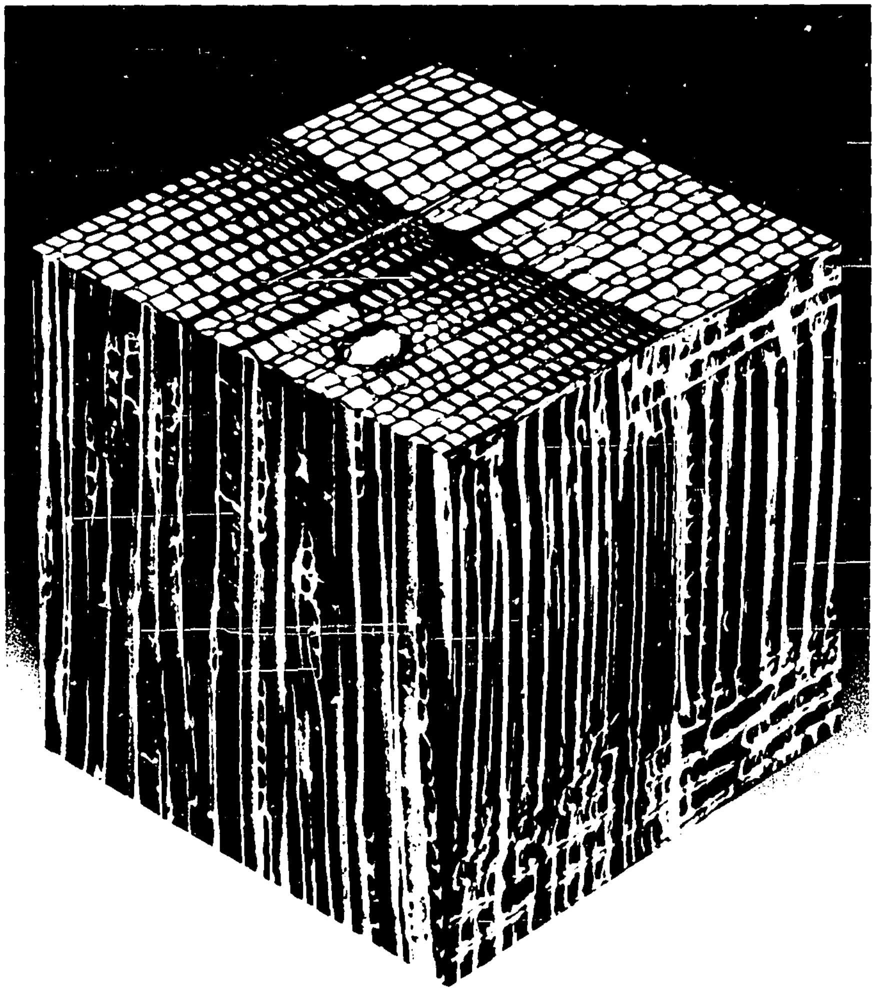


FIG. 2

An enlarged view of a 0.025 in. cube of black spruce (3) shows the tracheids running in the direction of the vertical axis of the tree. The annual ring, separating the larger early-wood fibres to the right from the smaller late-wood fibres, indicates the tangential direction.



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was fabricated from laminated wood. Much of the technical literature relevant to this development is still classified.

The ability of wood to damp vibrations is an important requisite for both airframe and airplane propeller construction and this requirement prompted studies on the comparative damping properties of several wood species (5). Vibration damping is also a highly desirable property of wooden skis and one which manufacturers of laminated metal skis have only recently been able to emulate successfully. This ability of wood, a typical polymer composite, to absorb kinetic energy and dissipate it as heat, is an important facet of its viscoelastic behaviour. Another well known example of this behaviour, which has evolved over the centuries as traditional art, is the ability to bend and twist steamed wood into predetermined shapes and permanently set them by cooling. Liquid ammonia is an even more effective plasticising agent than steam. Wood treated with liquid ammonia can be contorted into very dramatic permanent shapes (6).

Recent advances in polymer science have provided such a basic understanding of the structural group functions in many synthetic polymers that it is now possible to tailor-make polymers which have a predetermined combination of mechanical properties. It is an almost inevitable consequence of such progress that the properties of many natural polymers are now being re-examined in a different light. Indeed, several recent studies on wood, prompted in part by findings on synthetic polymers, have given new insights into its mechanical behaviour (7,8,9). It is a commentary on the novelty of these findings that an authoritative text on the mechanical properties of wood published in 1953 contains no mention of them.

Goring and his colleagues have studied the thermal softening of dry and water-plasticised powdered samples of wood species and extracted wood components. Thermal softening of powder samples is accompanied by an abrupt change in slope of the powder volume-temperature curves at the softening temperature. Dry isolated lignins and hemicelluloses were found to soften at temperatures ranging through 127-193°C (10). Dry powdered spruce, birch and poplar soften at approximately 230°C (11). These temperatures were thought to be glass transition temperatures - characteristic temperatures at which amorphous polymers undergo major structural transition from an almost elastic glassy state to an almost elastic rubbery state (12). When water was added to the powdered materials the transition temperatures were lowered by an amount ranging through 50-150°C. This behaviour is similar to that exhibited when plasticising agents are added to amorphous polymers.

The importance of thermal softening of lignin in the mechanical pulping of wood has long been recognised (3,13, 14,15). Several years ago, Asplund (16) developed a process for the production of coarse board-grade pulps in which wood chips were heated in pressurized steam to about 180°C and then subjected to attrition under these conditions. In this process, defibering of the wood chips is thought to be greatly assisted by softening of the lignin in the middle lamellae between the tracheids. The practical possibility of defibering wood chips under steam pressure at temperatures between 100-200°C to produce high grade pulps for the manufacture of printing papers is currently being investigated (17). In this regard it is desirable to extend Goring's work and obtain similar data on whole woods.

Such an extension will require a somewhat different experimental approach. Several other physical properties besides volume show an abrupt change with temperature in the region of a glass transition. Two properties which have been examined quite frequently for the determination of transitions in solid polymers are the elastic moduli and the mechanical damping. Elastic moduli generally show a sharp drop of about three decades from about 10^{10} dynes/cm^2 to 10^7 dynes/cm^2 and the mechanical damping of low frequency oscillations shows a sharp peak at the transition temperature. A typical well known example of this behaviour is shown for poly-methyl methacrylate in Fig. 3 (18). The main glass transition occurs at 125°C and a broad secondary transition occurs around 40°C. The latter transition arises from the motion of the carbo-methoxy side groups which become mobile at a lower temperature than the main chain. These data were obtained in low frequency torsional oscillations at about

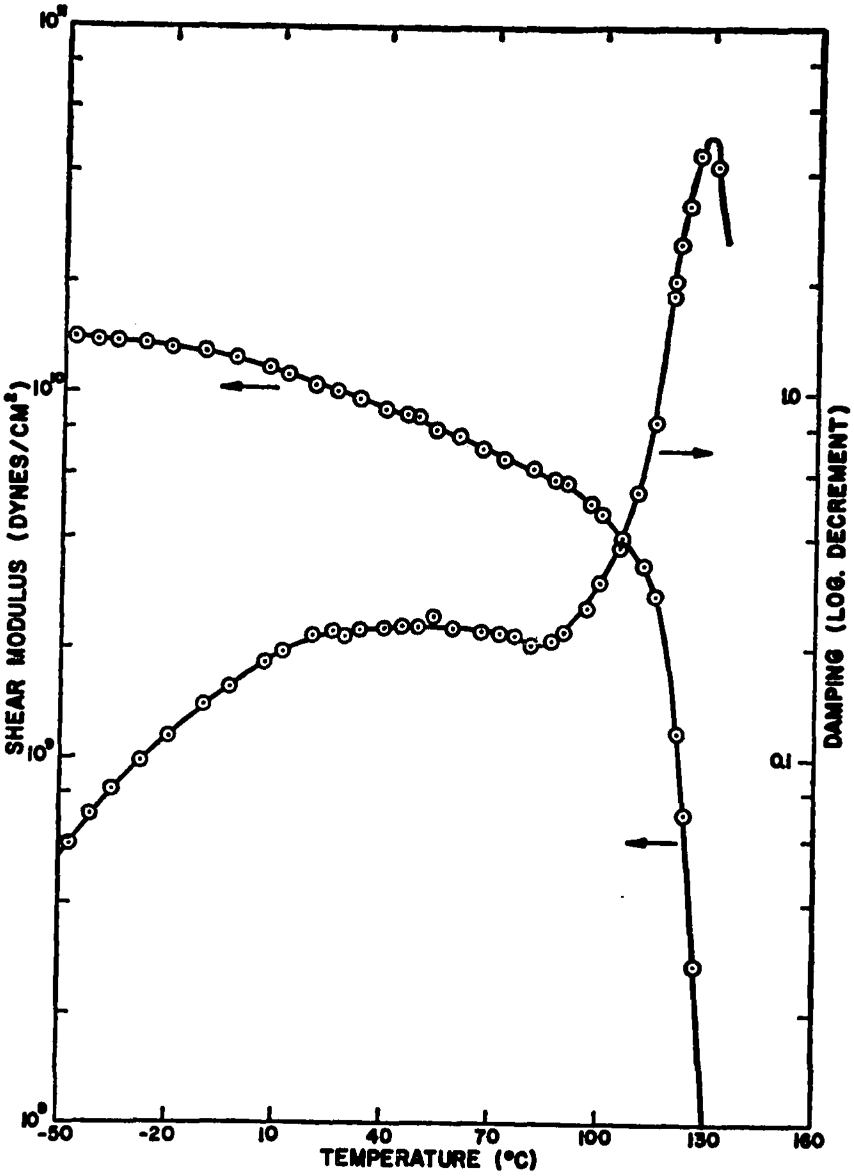


FIG. 3

Variation of the elastic shear modulus and the logarithmic decrement with temperature for polymethyl methacrylate. The main glass transition is indicated by the peak in the logarithmic decrement curve and the abrupt decrease in the elastic shear modulus at 125°C (See text).

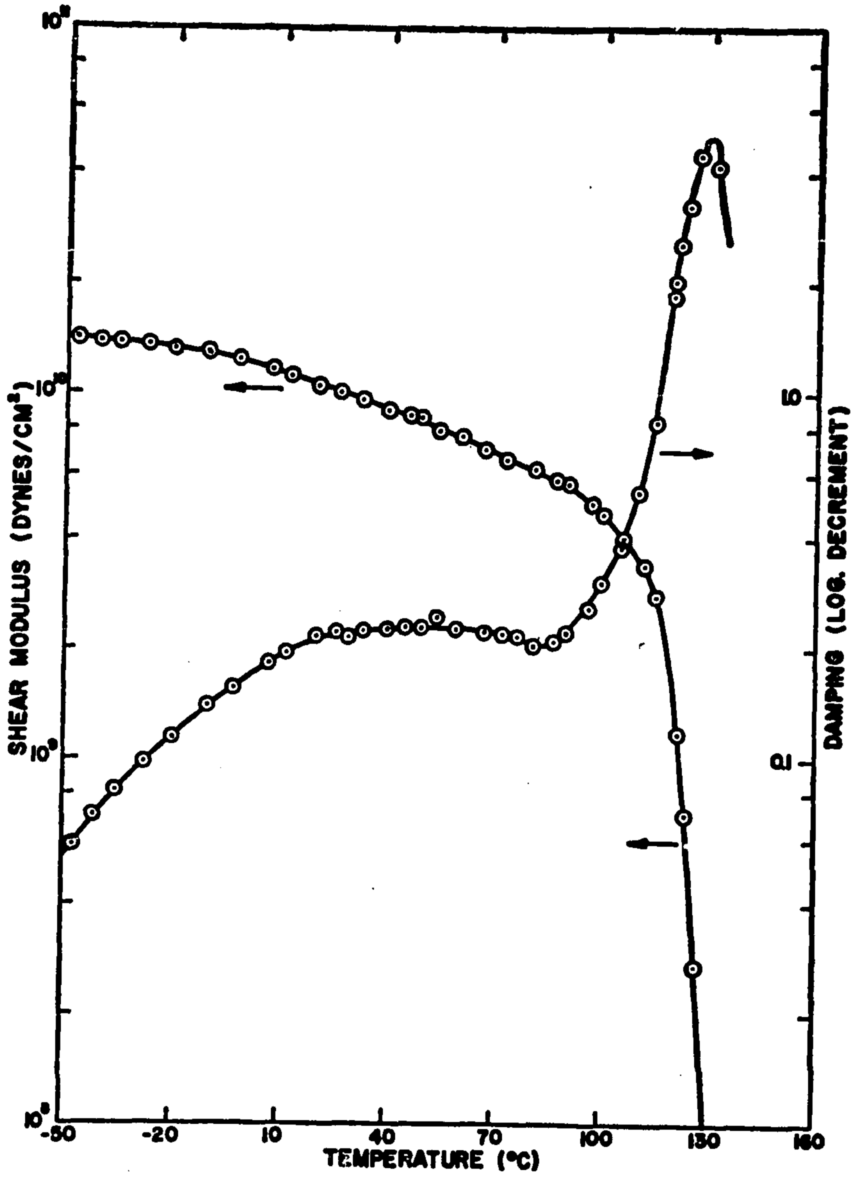


FIG. 3

Variation of the elastic shear modulus and the logarithmic decrement with temperature for polymethyl methacrylate. The main glass transition is indicated by the peak in the logarithmic decrement curve and the abrupt decrease in the elastic shear modulus at 125°C (See text).

10 c.p.s. and it should be noted that higher frequency vibrational methods will measure a glass transition temperature which is higher by about 7°C per decade increase of frequency.

Conversely, as previously indicated, plasticisers lower the transition temperature and broaden the transition range. In general, the lower the solubility of the plasticiser in the polymer the broader is the transition range (19).

The torsion pendulum is eminently suited for studying the dynamic mechanical properties of wood through the required temperature range. Small specimens can be employed to offset the inherent variability of wood properties and the specimen can be surrounded by almost any desired environment. Furthermore, the test is non-destructive and hence the same specimen can be used throughout the entire temperature range. This does not, of course, preclude the possibility of irreversible changes or chemical reactions, induced by the environment, occurring in the wood. Although the experimental technique employing the torsion pendulum is well accepted for the determination and examination of transition phenomena in high polymers it has never been used for similar studies on solvent-swollen wood.

The effect of temperature on the tensile strength of moist spruce and birch (20,21) and on the shear strength of moist birch (22) has been investigated through the range 20-

200°C. In all cases, the strength decreases with increasing temperature. Changes of strength are reversible up to 170°C and irreversible above 170°C. The nature of the fracture surface changes from a predominantly cellulosic one below about 120°C to one that is highly lignified above 170°C. There is no evidence of an abrupt change in the strength properties or the nature of the fracture surface, although the results strongly suggest that something drastic occurs at about 170°C. Lagergren, Rydholm and Stockman (20) suggest that changes occurring in the temperature range 160-180°C may not be due entirely to lignin softening as previously thought and speculate upon other possible causes. Goring and Baldwin (11) find that moist untreated powdered spruce and birch show a glass transition in the temperature range 170-190°C although they do not associate this transition with any physical or chemical process. It is possible that studies of glass transition phenomena in whole wood samples of these species may resolve some of the outstanding questions regarding the physical and chemical changes which give rise to thermoplasticity and failure.

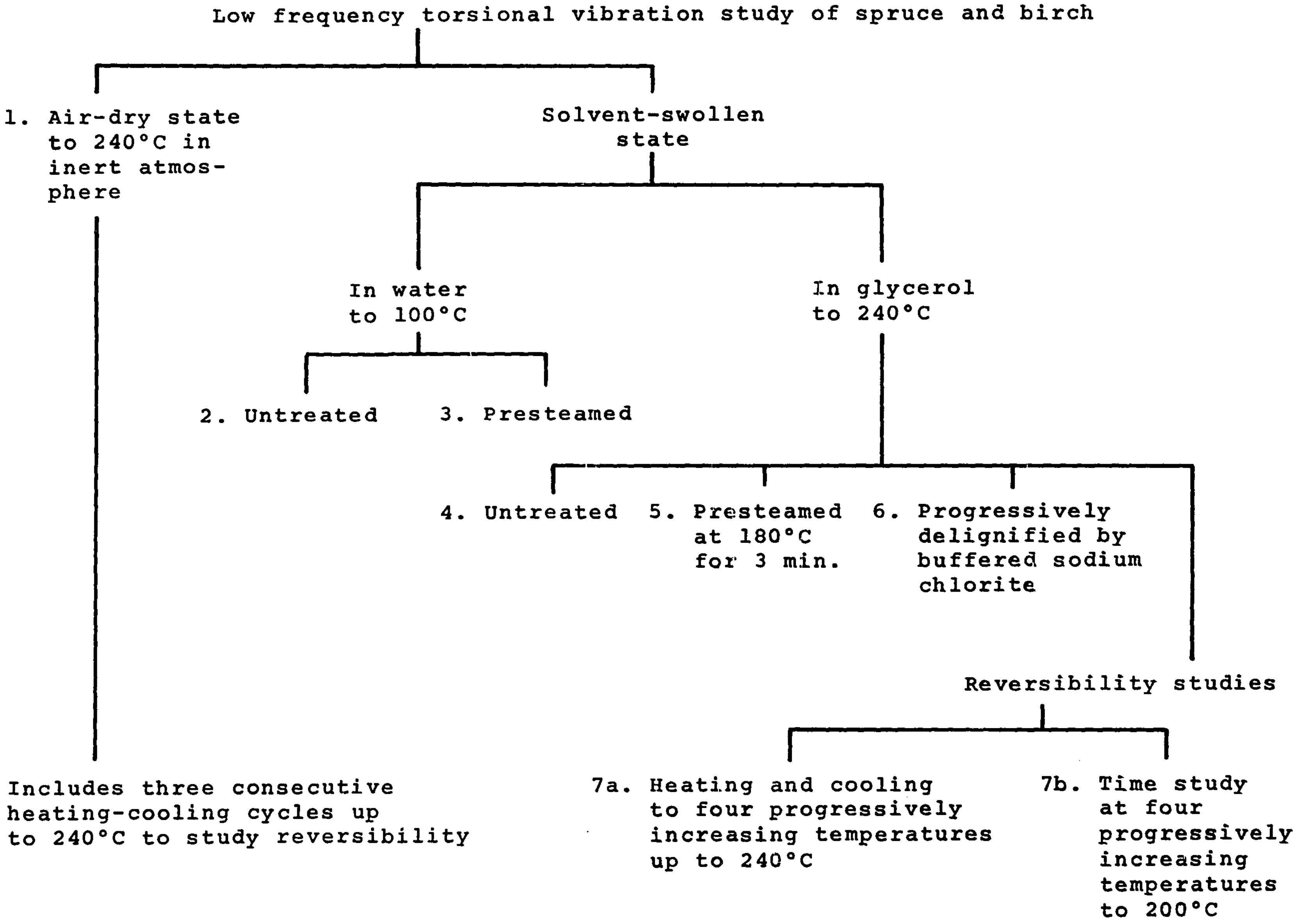
Aims and Scope of Investigation

The chief purpose of this investigation is to study the effect of temperature on the mechanical properties of wood. A typical softwood, eastern black spruce, and a typical hardwood, white birch, were selected for this study because of their commercial importance in the Canadian pulp and paper industry.

Selected mechanical properties of these wood species were measured using a torsion pendulum. Free vibration methods have been used frequently to study the mechanical properties of air-dry wood at room temperature but never to my knowledge have they been used for studies on solvent-swollen wood at higher temperatures. Apart from adding to the basic knowledge of the physical properties of wood, the results of these studies should provide useful guidelines for the thermal processing and thermo-mechanical pulping of these wood species.

It is proposed to divide the investigation of mechanical properties into seven parts as shown in the chart.

1. The effect of temperature on the elastic shear modulus parallel to the grain, and the mechanical damping of dry spruce and birch. Results obtained in these tests will be used to assess the experimental technique and provide a comparison with similar data in the literature.
2. Investigation of the effect of temperature on untreated water-swollen specimens.
3. To determine whether lignin softens by pre-steaming at 180°C for 3 minutes and, if so, whether such softening is accompanied by irreversible changes, a series of experiments will be conducted on pre-steamed specimens



Low frequency torsional vibration study of spruce and birch

1. Air-dry state to 240°C in inert atmosphere

Includes three consecutive heating-cooling cycles up to 240°C to study reversibility

Solvent-swollen state

In water to 100°C

2. Untreated

3. Presteamed

In glycerol to 240°C

4. Untreated

5. Presteamed at 180°C for 3 min.

6. Progressively delignified by buffered sodium chlorite

Reversibility studies

7a. Heating and cooling to four progressively increasing temperatures up to 240°C

7b. Time study at four progressively increasing temperatures to 200°C similar to those in Section 2.

4 and 5. To test swollen specimens above 100°C at atmospheric pressure, glycerol will be used as a plasticiser. Glycerol contains a large number of hydroxyl groups and is known to swell wood in a manner similar to that of water. Untreated and pre-steamed specimens previously tested in water will also be tested in glycerol. These data will allow a comparison of the effect of water and glycerol as plasticisers up to 100°C. Furthermore, data will be obtained using glycerol up to 240°C.

6. The effect of temperature on the mechanical properties of progressively delignified specimens of spruce and birch in swollen state will be investigated. Buffered sodium chlorite, a chemical agent which specifically dissolves lignin, will be used as the cooking liquor.

7. Irreversible changes that occur in untreated glycerol-swollen wood at high temperatures should depend upon the temperature level at which the specimen is held and the length of time it is maintained at that temperature. Thus, in one series of tests, a specimen will be held at predesignated progressively higher temperatures for various lengths of time. In a second series of

tests, a specimen will be subjected to one heating and cooling cycle at each of several predesignated and progressively higher temperature levels. These studies will be conducted at the end of the investigation since temperatures chosen will depend upon the results of the previous tests.

DESCRIPTION OF APPARATUS

Measurements of elastic shear modulus and logarithmic decrement of damping of various wood specimens through the temperature range 0-250°C were made using a direct recording torsion pendulum manufactured by Plas-Tech Corporation, Natick, Mass., U.S.A. Conditions of measurement conform to the requirements of A.S.T.M. D2236-64T (23).

The equipment which is based on a patented design (24), consists of:

(1) A torsion pendulum

(2) A Sanborn direct writing oscillographic recorder (Model 7701A) equipped with a carrier preamplifier (Model 8805A)

(3) A Leeds and Northrup Speedomax temperature indicator, recorder and proportionating controller for temperature control through the range -200° to +300°C

(4) Gas and liquid phase thermostats.

Torsion Pendulum

Fig. 4 is a photograph of the torsion pendulum. The pendulum is mounted on a rigid test frame consisting of two chrome-plated brass sections thermally insulated from each other by a transite disc.

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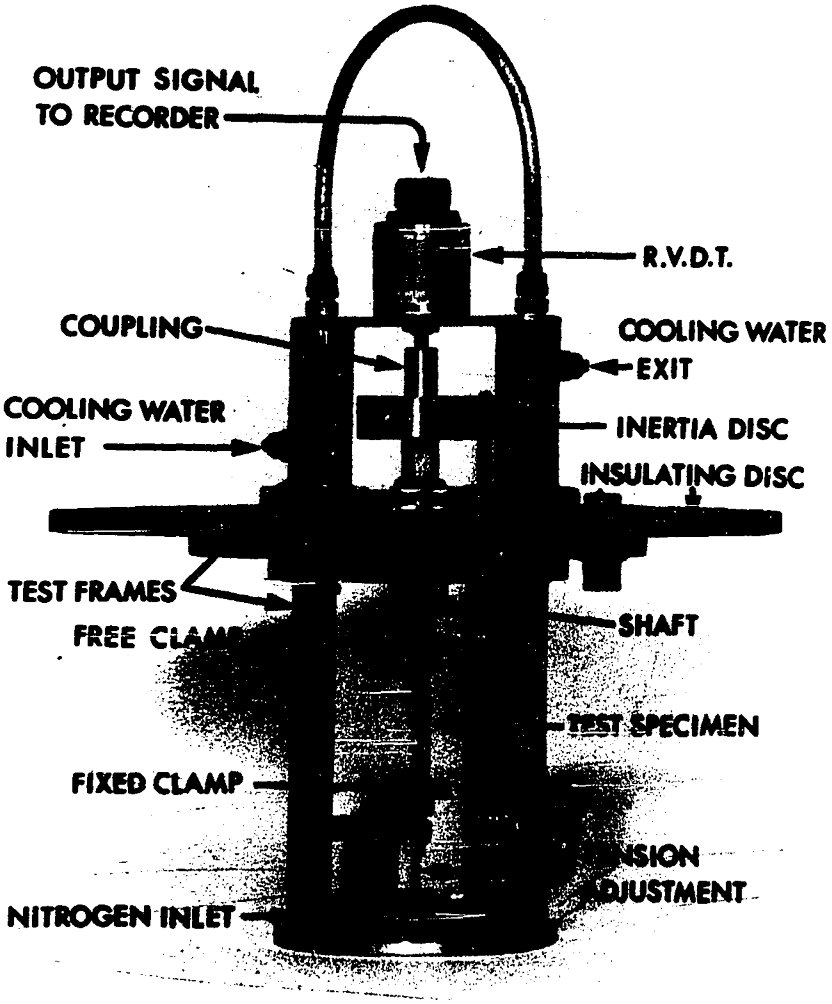

FIG. 4

Front view of the torsion pendulum.
(See text for description).

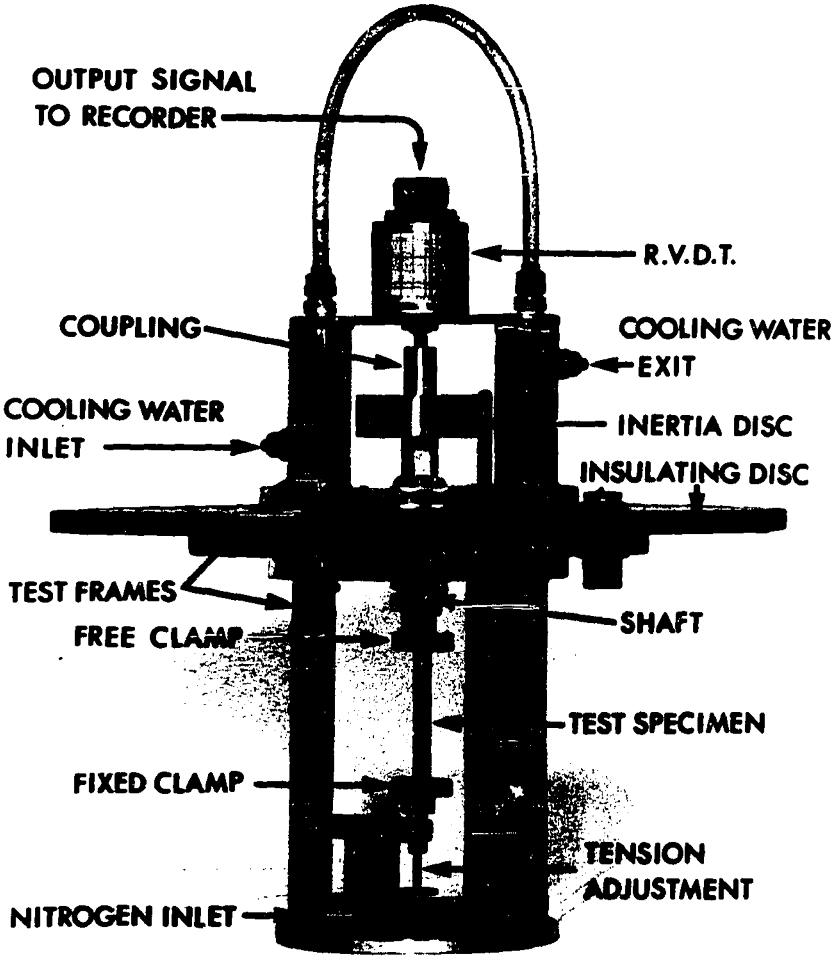

FIG. 4

Front view of the torsion pendulum.
(See text for description).

former (R.V.D.T.) is rigidly mounted on the top frame, part of which is hollow and water cooled to prevent thermal damage to the transducer during the high temperature tests.

The test specimen is held between two steel clamps. The upper clamp is welded to a 0.25 in. diameter steel shaft which passes through clearance holes in both sections of the frame and the transite disc and is solidly coupled to the shaft of the R.V.D.T. This clamp is free to rotate about the longitudinal axis of the R.V.D.T. shaft.

A split inertia disc is mounted on the shaft and held firmly against the coupling by a nut. A small collar on the disc fits into a recess in the coupling to prevent lateral movement. The moment of inertia of the whole assembly can be varied to suit the experimental requirements by mounting a disc of suitable moment of inertia. Several discs, each with a different moment of inertia, are available.

The lower clamp is pinned to a bar which in turn is pinned to a bracket mounted rigidly to the bottom plate of the lower frame. This allows the central point of the clamp to move colinearly with the longitudinal axis of the R.V.D.T. without lateral movement. Thus, the specimen may be held free from longitudinal tensile strain which may arise from deformations due to either thermal expansion or oscillatory shear.

The upper clamp, extension shaft and lower clamp assembly were considered torsionally rigid for the small strains to which the less rigid specimen was subjected during the experiment and it was assumed that the R.V.D.T. measured only the angular displacement of the specimen.

Temperature Control

1. Nitrogen Gas Thermostat

Some experiments were conducted in a temperature controlled inert atmosphere of dry nitrogen gas.

For temperatures above ambient an annular chrome-plated brass sleeve is screwed on to the bottom frame as shown in Fig. 5 and an insulated 500 watt electrical heating tape is wound over the sleeve. A copper-constantan thermocouple is located immediately adjacent to the test specimen to monitor its temperature. This entire assembly is then lowered into a thermally insulated stainless steel chamber so that the insulating disc rests on the top lip of the chamber. Nitrogen gas at 3 p.s.i. is admitted through a perforated brass ring surrounding the lower clamp assembly. The rate of flow of the nitrogen gas is controlled by a small needle valve to a value in the range of 4-8 cubic feet per hour. Higher flow rates caused large temperature fluctuations.

Using this system, temperature control could be maintained within ± 0.5°C through the range 20-240°C.

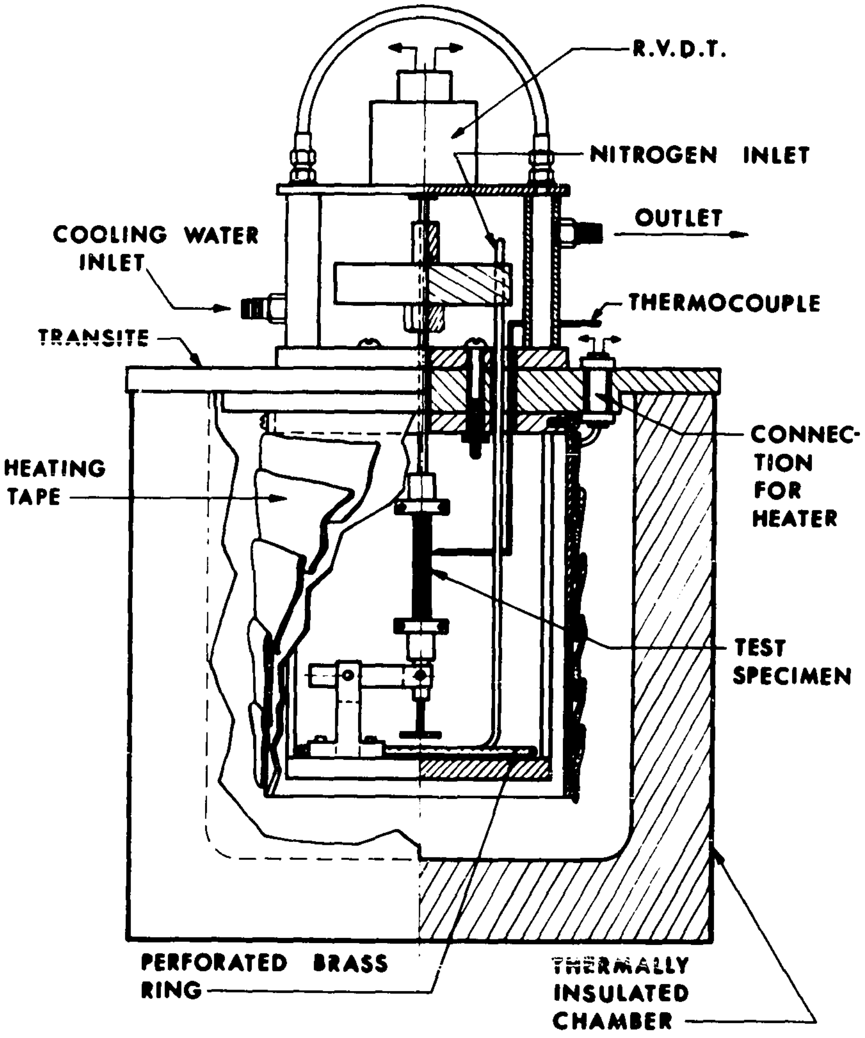

FIG. 5

Sectional schematic view of the torsion pendulum mounted in the gas thermostat. The lower frame of the pendulum is surrounded by insulated heating tape wound over an annular sleeve. Temperature is monitored by a thermocouple adjacent to the specimen.

Temperatures below ambient are obtained and controlled by feeding liquid nitrogen under 5 p.s.i. pressure from a dewar through the perforated ring.

A schematic representation of the temperature recording and controlling system is shown in Fig. 6. The e.m.f. generated by the thermocouple is matched through the appropriate range card against the e.m.f. of the measuring potentiometer circuit. The difference between these two e.m.f.'s produces an "error" current which is amplified and drives a reversible balancing motor. This in turn moves the potentiometer slider in the appropriate direction to obtain a null balance. It also moves the temperature indicator and recorder pen, attached to the slider, to give a temperature read-out. Fig. 7 is a photograph of the instrument showing the temperature read-out and recorder.

The slide wire of the control potentiometer is mechanically linked to the temperature indicator through the balancing motor. Thus, when the measured temperature does not coincide with the desired temperature indicated by the set point on the control potentiometer an error current is produced. This current is used to actuate either a relay or solenoid valves, shown in Fig. 6, which respectively control the heating or cooling of the gas stream to approach the desired temperature.

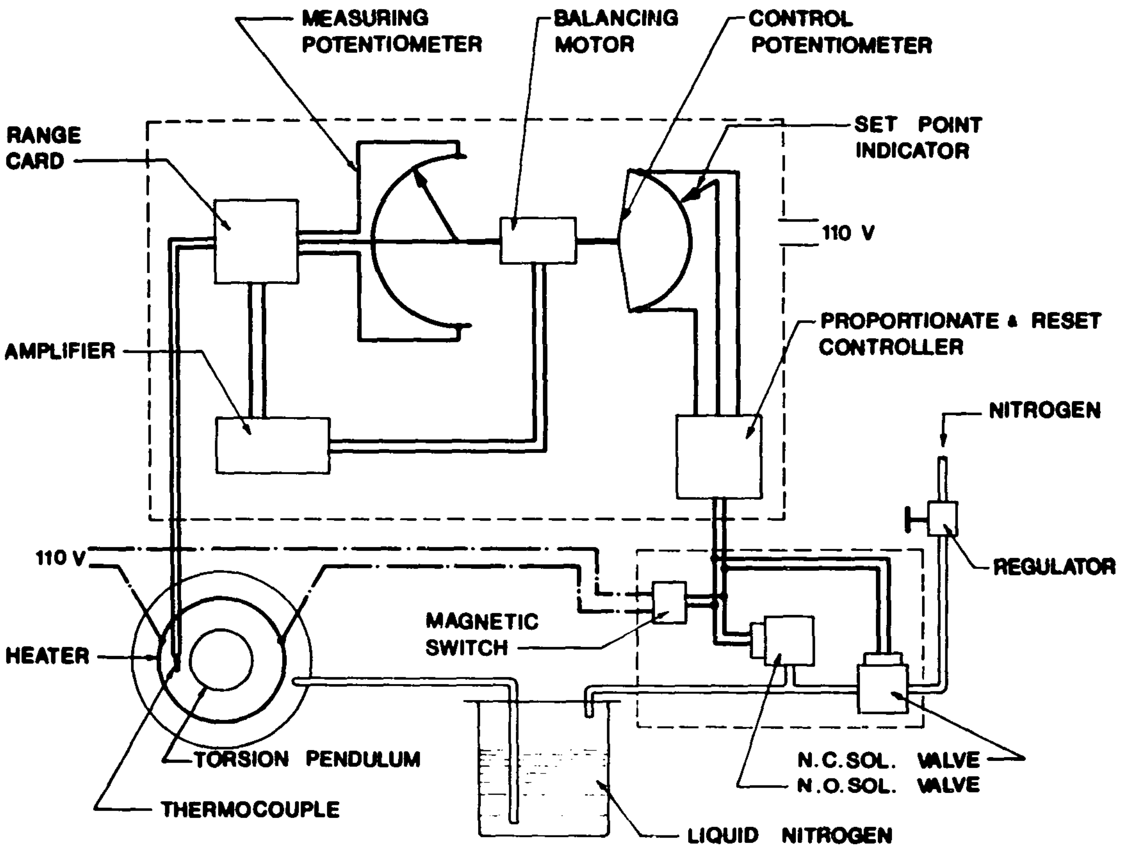

FIG. 6

Schematic representation of the temperature-control circuitry. Voltage generated by the thermocouple is matched against the measuring potentiometer. When the indicated temperature is not the same as the one required by the set point indicator, the control potentiometer generates a directional signal to switch the heating or cooling circuit on or off as required.

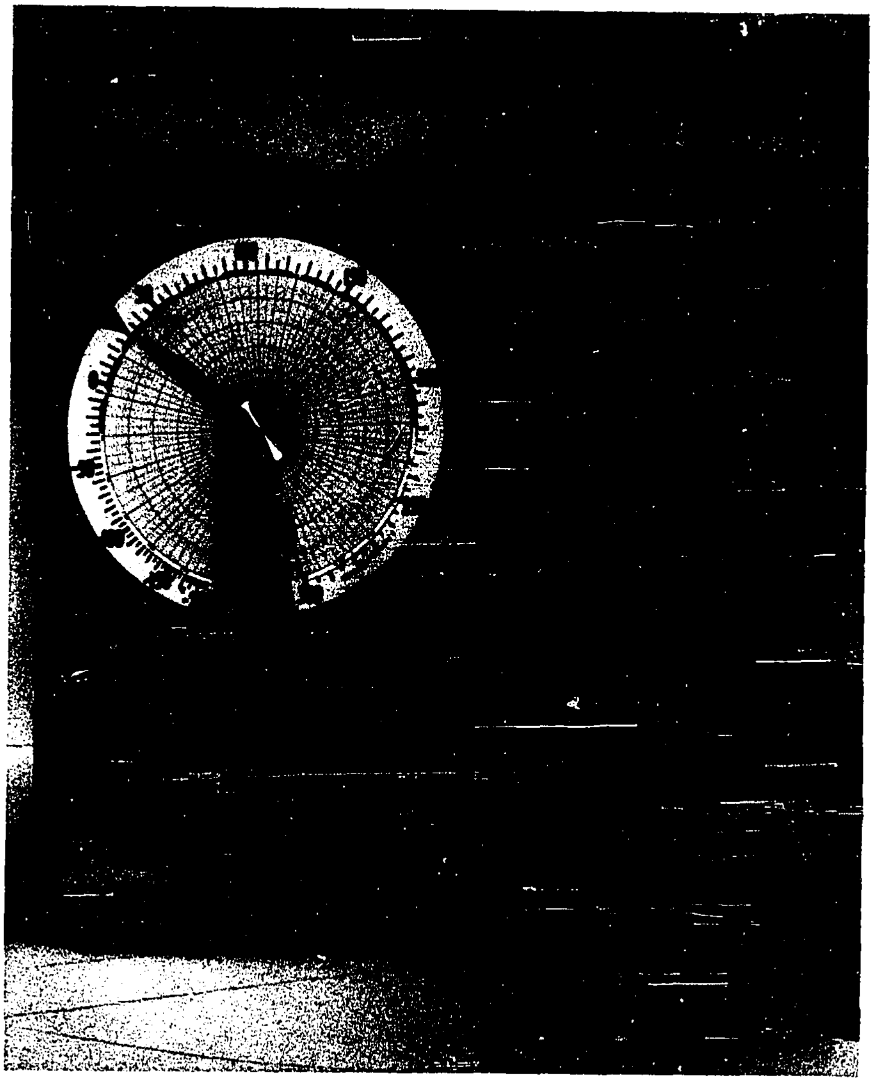

FIG. 7

Front view of the "Speedomax" temperature recorder and controller. Control knobs at the bottom were adjusted for optimum temperature control.

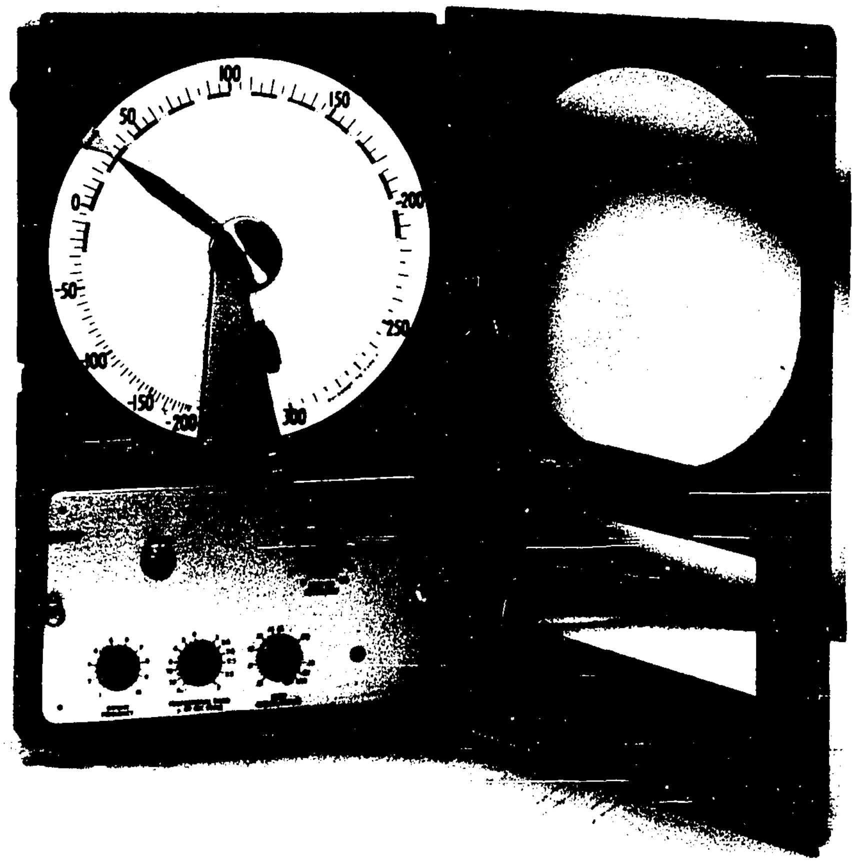

FIG. 7

Front view of the "Speedomax" temperature recorder and controller. Control knobs at the bottom were adjusted for optimum temperature control.

2. Liquid Bath Thermostat

Most of the experiments were conducted with specimens immersed in a temperature controlled liquid environment.

Fig. 8 is a photograph of the thermostat. The system consists of a 12 in. diameter x 12 in. high pyrex glass jar insulated with asbestos tape and filled with the desired thermostatic liquid. This jar rests on a stand into which are built enclosed electrical control relays. Two coil-heaters, one 1,000 watts and one 750 watts, shaped to the inside diameter of the jar, are immersed in the liquid to provide the heat source. A mercury contact thermometer-thermoregulator immersed in the liquid controls the power to the 1,000 watt heater through the power relay, according to the thermometer setting. The 750 watt heater is manually controlled. Arrangements were also available to circulate cooling water through coiled copper tubing immersed in the thermostatic liquid to reduce the bath temperature.

Water, 50-50 water-glycerine mixtures, and 100% reagent grade glycerine were used as thermostatic liquids. The entire unit was located in a fume hood to conduct away noxious glycerine fumes produced above 130°C. The torsion pendulum was lowered into the liquid bath and supported by the transite disc resting on the edge of the pyrex jar. The level of the thermostatic liquid was continually adjusted so as to completely immerse the test specimen. A bent copper tube was provided to siphon off excess liquid due to thermal

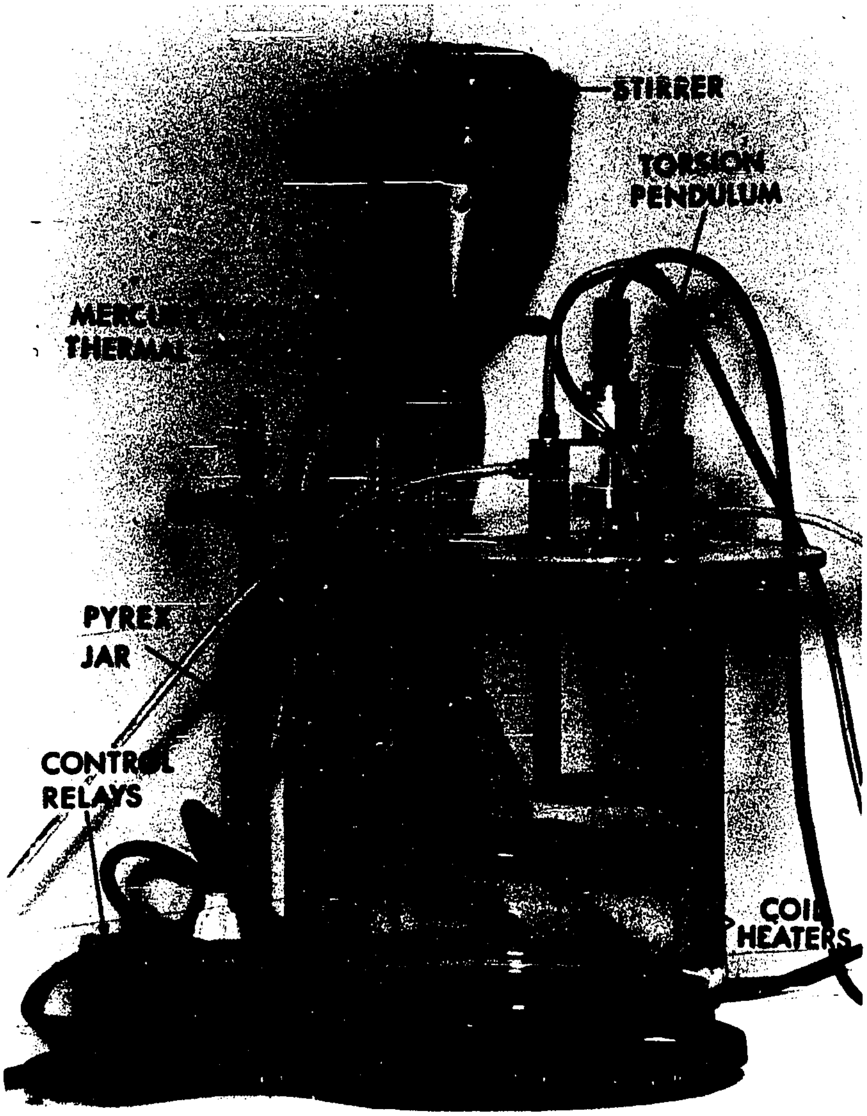

FIG. 8

Front view of the liquid bath thermostat. Thermal insulation has been removed from the glass jar to give an inside view.

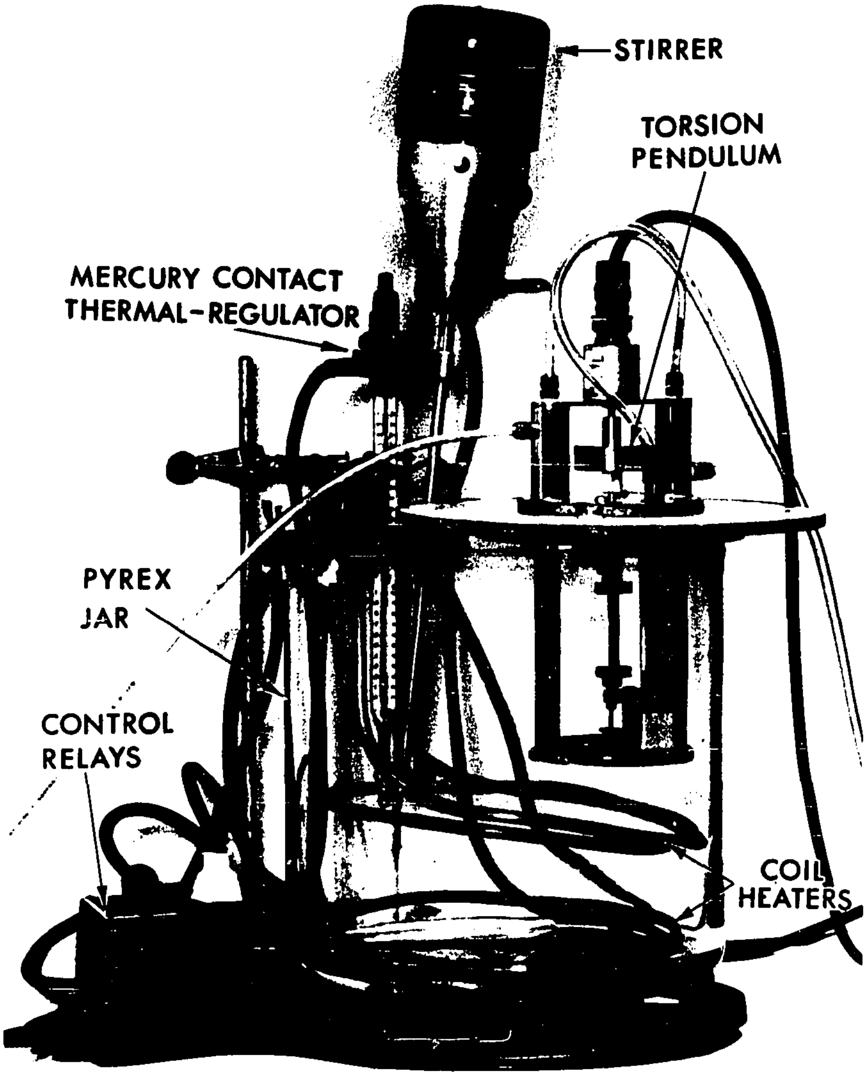

FIG. 8

Front view of the liquid bath thermostat. Thermal insulation has been removed from the glass jar to give an inside view.

expansion as the temperature was raised and liquid was added as the bath was cooled in order to maintain the liquid level just above the upper clamp.

The temperature was measured by a copper-constantan thermocouple and recorded on the Speedomax unit. The bath temperature was varied in steps of either 4° or 5°C depending upon the total range of temperature to be investigated. The specimen was held at each temperature for 10 minutes prior to conducting measurements to ensure thermal equilibrium throughout the specimen. The time was determined from a series of preliminary tests.

PREPARATION OF TEST SPECIMENS

Test specimens were cut from clear samples of eastern black spruce (Picea mariana), donated by Kruger Pulp and Paper Co. Ltd., Bromptonville, Quebec, and samples of white birch (Betula papyrifera-Marsh), donated by Domtar Limited, Senneville, Quebec.

Pieces approximately 2.5 in. x 0.25 in. x 0.067 in. were cut from the sapwood. The 2.5 in. dimension was parallel to the grain and the 0.25 in. dimension was in the tangential direction. Spruce samples contained 2 or 3 growth rings and birch samples contained 1 or 2 growth rings. No effort was made to maintain the same early-late wood ratio in all specimens.

After inspection specimens were chosen which were free from cracks, splits or any unusual growth phenomena. They were stored until needed in polythene bags in a refrigerator.

Specimens selected for testing in the torsion pendulum were finished by gently abrading against wet 400 grit emery paper. All final dimensions were uniform to within ± 0.002 in.

Alcohol-Benzene Extraction

Most of the specimens were extracted for 36 hours in a 40-60 solution of alcohol-benzene in a Soxhlet as seen in Fig. 9. Extracted specimens were washed in several changes of water for 24 hours.

Delignification with Sodium Chlorite

Spruce and birch specimens were partially delignified to differing yields according to a method devised by Wise (25), and modified by Timell (26), for the preparation of wood holocellulose.

Thirty-five specimens, including ten hand-finished specimens, of each species were allowed to air-dry at room temperature for 48 hours. For each species the specimens were divided into seven groups as follows. Five groups had each two hand-finished specimens for testing, two unfinished specimens for yield determination and one unfinished specimen for

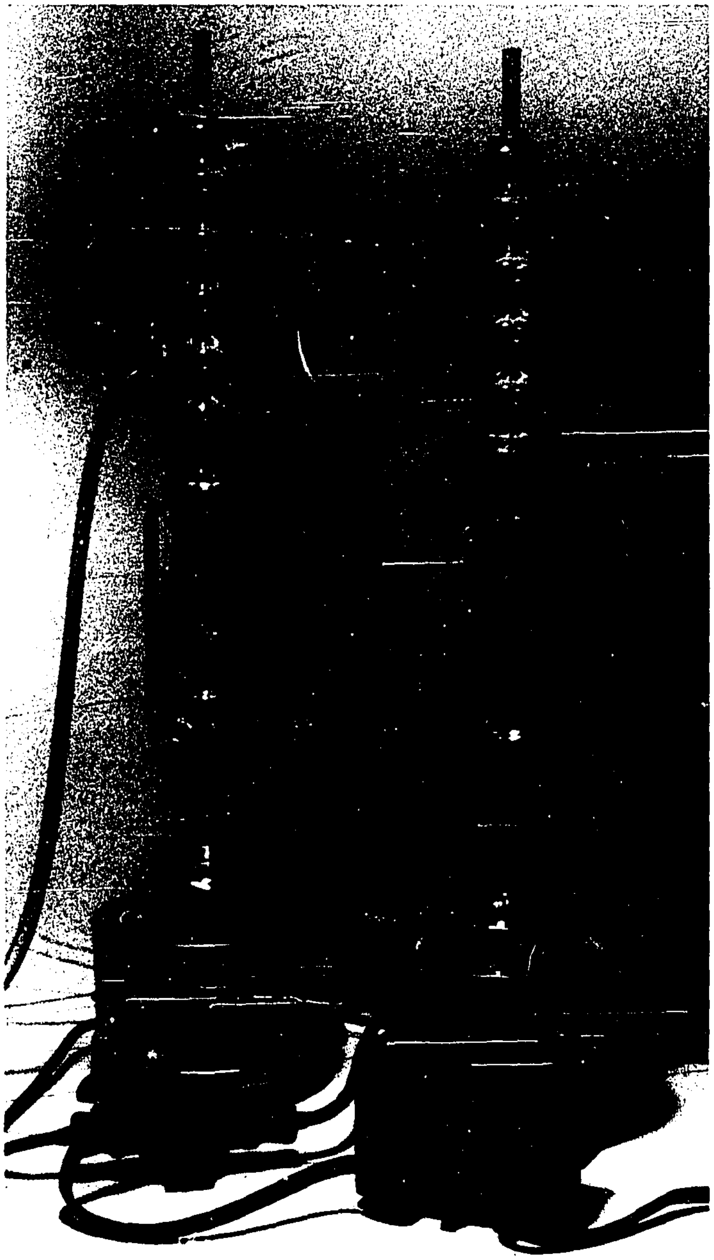

FIG. 9

Soxhlets used for alcohol-benzene extraction of wood specimens.

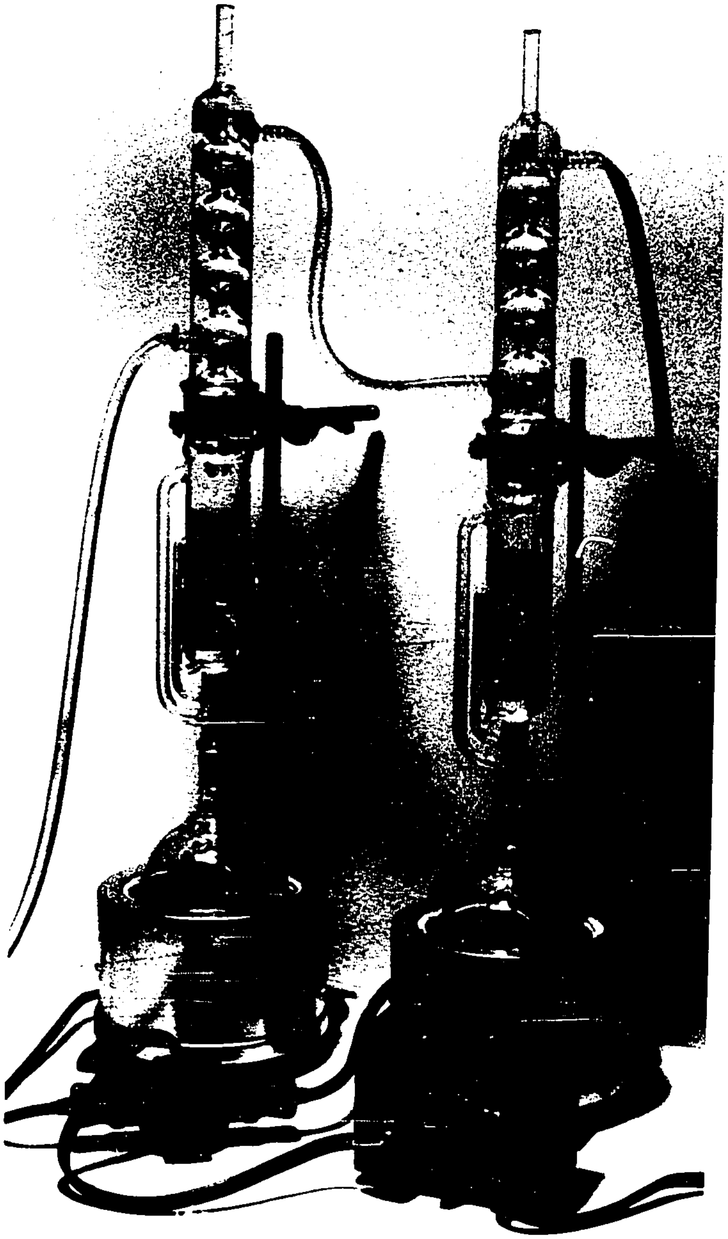

FIG. 9

Soxhlets used for alcohol-benzene extraction of wood specimens.

lignin determination in the UV microscope (27). Two additional groups each contained five unfinished specimens. One group was employed for the determination of moisture content and the other for measurement of the extractive content following alcohol-benzene extraction.

After air drying for 48 hours, each group was weighed. The seventh group was heated to constant weight in an oven at 110°C and the moisture content of all samples of that species was then assumed to be identical with that of this group. Thus, as may be seen from Table I, the moisture content of the spruce specimens was 6.2% and that of the birch specimens was 7.8%. The remaining samples in groups 1-6 were extracted in alcohol-benzene for 36 hours and the loss of weight due to extraction of the sixth group was used to determine the extractive content. The extractive content of the spruce and birch specimens determined in this manner was 0.8% and 1.2% respectively.

After extraction, each of the remaining five groups was placed in a separate test tube containing 50 ml of an aqueous solution containing 20 gm/litre sodium chlorite buffered with 0.35 ml of glacial acetic acid. The test tubes were placed in a basket attached to a shaking unit as seen in Fig. 10 and immersed in a water thermostat at 50°C. Cooking liquor was changed every four hours and samples were removed after cooking times ranging through 6-48 hours as shown in Table I. After removal, specimens were washed in

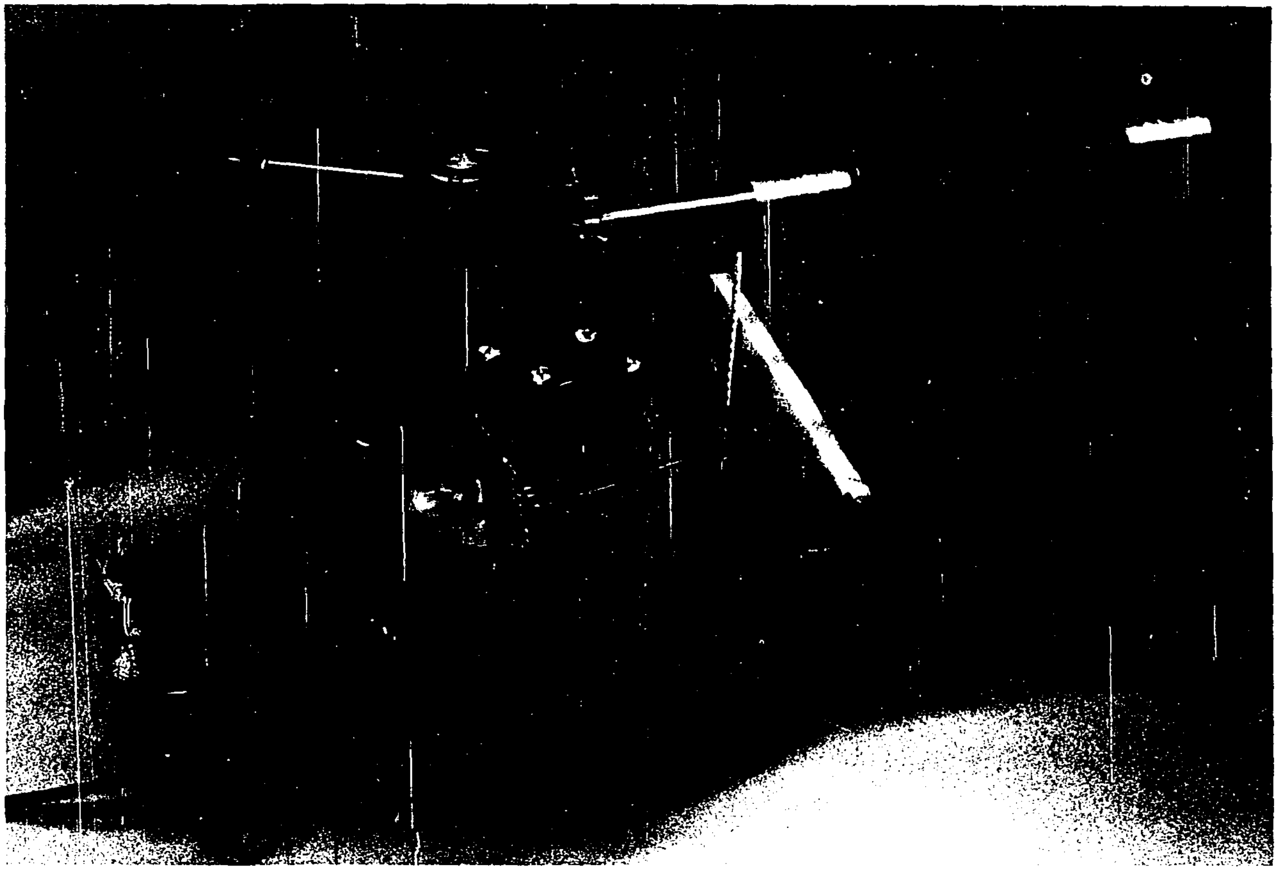

FIG. 10

View of the delignification apparatus. Test specimens are placed in the test tubes containing buffered sodium chlorite solution. The test tube container is continuously agitated.

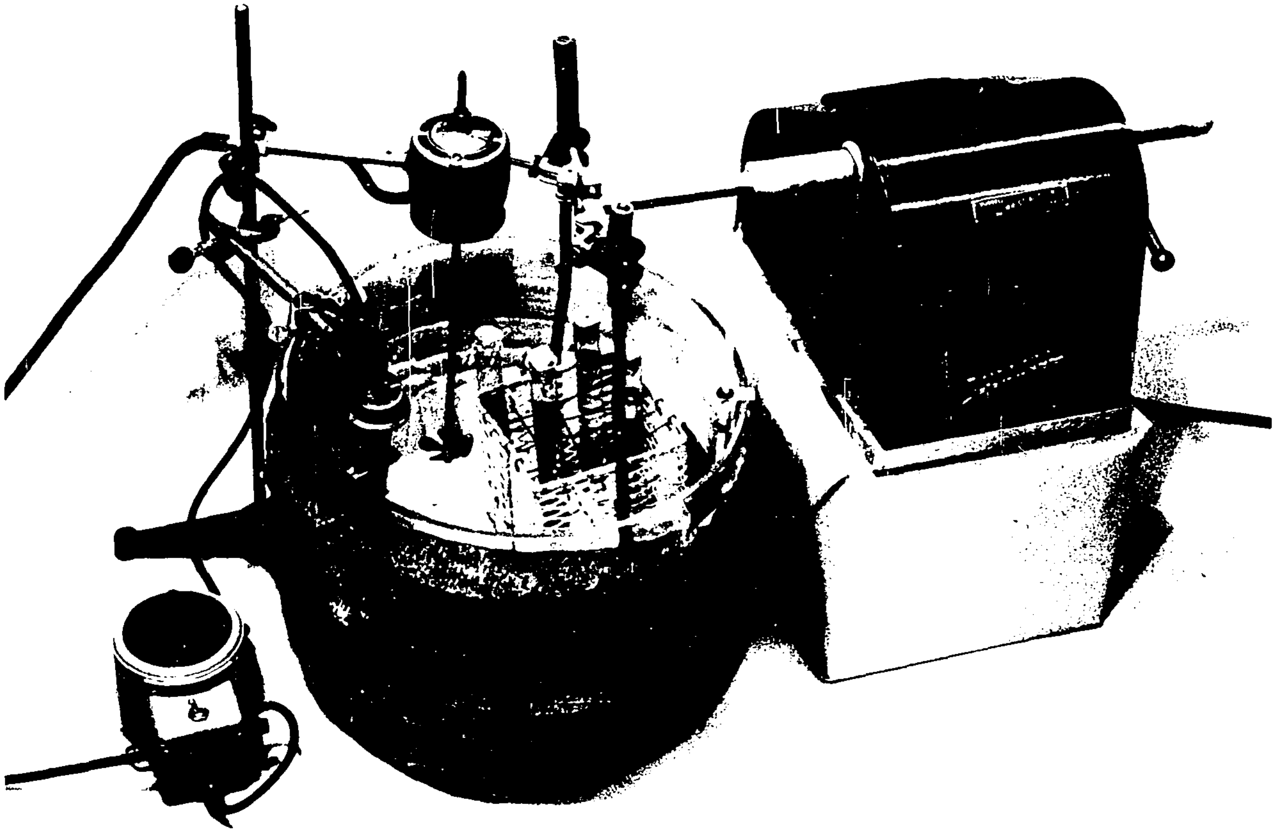

FIG. 1[illegible]

View of the delignification apparatus. Test specimens are placed in the test tubes containing buffered sodium chlorite solution. The test tube container is continuously agitated.

distilled water for 24 hours using 4-5 changes of water. Two samples for yield determination were oven dried and the per cent yield was determined on the basis of the extracted oven-dry weight of the sample prior to cooking.

Experimental data describing the delignification of the spruce and birch samples are given in Table I.

Prior to adopting the delignification procedure described above, a series of cooks was conducted under identical conditions except that shorter cooking times, of the order of 1-10 hours, were employed at 70°C. It was noted that specimens cooked under these conditions showed surface defibration even when gently handled. Furthermore, when such specimens were mounted in the torsion pendulum and heated to 200°C, extensive defibration occurred at the edges of the specimen. This observation strongly suggested that delignification had not occurred uniformly throughout the specimen. This was confirmed qualitatively by gently rolling the specimen between the fingers; surface fibres came away very readily but a point was reached where no further fibres could be removed even with harsher treatment. A quantitative measure of the non-uniform distribution of the residual lignin was obtained by photographing ultra-thin sections cut from the centre of the specimen in ultraviolet light under standardized conditions and conducting densitometric analyses on the photographic negatives.

Uniform delignification throughout the specimens was obtained by employing longer cooking times at the lower temperature of 50°C, and the uniformity was confirmed quantitatively by the U-V photographic method (27).

EXPERIMENTAL

The upper face of the lower clamp was positioned parallel to, and at a distance of 2 in. from, the lower face of the upper clamp with the aid of a machined steel gauge. The movable jaw of each clamp was unscrewed and one screw of the lower clamp was completely removed so that the test specimen could be inserted without disturbing the preset position of the lower clamp. When the specimen had been centrally positioned and aligned with respect to the axis of the R.V.D.T. the clamps were tightened and the final spacing was checked with the gauge.

After insertion of the test specimen the oscillographic recorder indicator was positioned at the centre of the chart by adjusting resistance and capacitor controls to balance out the effect of electrical impedance. A trace along the centre line of the chart represented the unstrained condition of the test sample.

The test specimen was put into torsional oscillation by turning the inertia disc lightly by hand and releasing. This damped oscillatory motion was converted by the R.V.D.T. into an electrical signal, proportional to the angular displacement, which was amplified and recorded on a strip chart moving at 50 mm/sec. When measurements were conducted in a thermostatted liquid bath the stirrer and the fume-hood motors were stopped during the test to avoid pick-up of mechanical vibration by the transducer. Fig. 11 shows a typical curve.

It may also be of interest to note that the maximum displacement on the chart (50 mm) represents an angular displacement of 2.5°.

Elastic Shear Modulus

The complex shear modulus G is defined as

$$G = G' + iG''$$

where G' is the elastic shear modulus

and G'' is the loss modulus.

The elastic shear modulus is given by (28)

$$G' = \frac{38.54\ LI}{bd^3\ \mu\ P^2}\ \text{dynes/cm}^2$$

where L = length of the test specimen between the clamps in inches

b = width of the specimen in inches

d = thickness of specimen in inches

I = polar moment of inertia of the oscillating system in $g \times cm^2$

P = period of one oscillation in seconds

μ = shape factor defined in terms of the ratio of width to thickness of the specimen. Typical values are given in Appendix I.

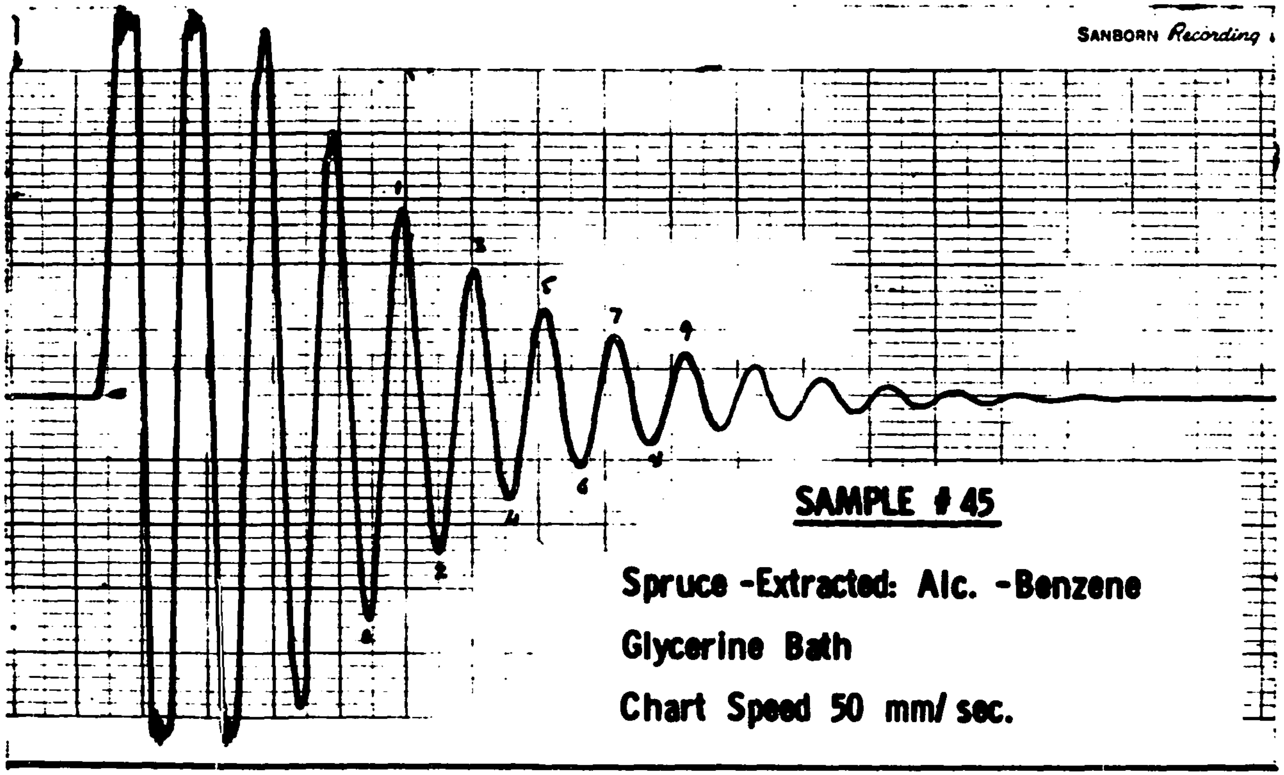

FIG. 11

A typical decaying oscillation is shown above. The height of a number of successive amplitudes, and the distance between some convenient number of peaks were measured. (See text for detailed calculations).

For the damping curve shown in Fig. 11

$L = 2.00$ $I = 884$

$b = 0.252$ $\mu = 4.25$

$d = 0.074$ $p = 0.214$

$$G' = \frac{38.54 \times 2 \times 884}{0.252 \times (0.074)^3 \times 4.25 \times (0.214)^2}$$

$$= 3.15 \times 10^9 \text{ dynes/cm}^2.$$

Log Decrement

The log decrement, Δ, is the natural logarithm of the ratio of any successive amplitudes.

$$\text{Thus,} \quad \Delta = \ln\frac{A_1}{A_3} = \ln\frac{A_3}{A_5} = \ln\frac{A_2}{A_4}$$

An equivalent measure is,

$$\Delta = \ln\frac{A_1 + A_2}{A_3 + A_4} = \ln\frac{A_3 + A_4}{A_5 + A_6}$$

where 1, 2 ... refer to the amplitudes such as shown in Fig. 11.

The second method of calculation was used since it inherently compensates for differences in the value of amplitude on either side of the centre line of the chart owing to any very slight misalignment of the specimen with respect to the axis of the R.V.D.T. or to a slight shift of the damping curve from the centre line of the chart during a single test.

An average value of ratios of amplitudes between 35 mm and 6 mm was taken and the natural logarithm of this average was designated Δ. The value of 35 mm for the upper limit of acceptable amplitude was chosen to ensure that measurements were within the response limit of the recorder. The lower limit of 6 mm was set to avoid excessive errors in measuring small amplitudes.

Thus, in the curve of Fig. 11.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
14.2	12.2	9.6	8.1	6.5	5.6	4.5	3.7

$$\frac{A_1 + A_2}{A_3 + A_4} = \frac{26.4}{17.7} = 1.49$$

$$\frac{A_3 + A_4}{A_5 + A_6} = \frac{17.7}{12.1} = 1.46$$

$$\frac{A_5 + A_6}{A_7 + A_8} = \frac{12.1}{8.2} = 1.48$$

$$\Delta = \ln\frac{1.49 + 1.46 + 1.48}{3}$$

$$= \ln 1.48 = 0.392$$

Graphs of elastic shear modulus and Δ were plotted as a function of temperature.

TABLE I

Experimental data for yield determinations after delignification of spruce and birch in buffered sodium chlorite solutions

Species	Group No.	Cooking Time hr.	Air-Dry Weight gm	Oven-Dry Weight gm	Yield %
Spruce					
	1	6	0.732	0.678	99.7
	2	18	0.603	0.505	90.2
	3	26	0.565	0.440	83.8
	4	34	0.627	0.472	81.0
	5	45	0.586	0.365	67.0
	6	Extractive Content	1.383	1.286	93.0
	7	Moisture Content	1.717	1.610	93.8
Birch					
	1	8	1.006	0.875	95.6
	2	16	1.063	0.896	92.7
	3	24	0.982	0.804	90.0
	4	34	1.023	0.825	88.6
	5	46	1.114	0.891	87.9
	6	Extractive Content	0.565	0.514	91.0
	7	Moisture Content	1.254	1.157	92.2

RESULTS

DYNAMIC MECHANICAL PROPERTIES OF SPRUCE AND BIRCH

1. In an Inert Atmosphere Through the Temperature Range 25-240°C

Fig. 12 shows the variation of elastic shear modulus and log decrement as a function of temperature for a black spruce specimen which had been extracted in alcohol-benzene for 36 hours, washed in distilled water and air-dried for 48 hours prior to testing. The sample was subjected to two cycles of heating and cooling in an inert atmosphere of dry nitrogen gas through the temperature range 25-240°C.

Although the specimen was dehydrated the shear modulus decreased gradually during the first heating cycle as the temperature was increased to 240°C. During the cooling cycle apparent values of shear modulus at any temperature were considerably lower than those obtained during the heating cycle. These low values were associated with damping curves which exhibited large variations in oscillation frequency. Furthermore, after cooling to room temperature the specimen was quite loose in the clamps. Upon tightening the clamps at room temperature a damping curve with a constant oscillation frequency was obtained.

Variation of the oscillation frequency is a necessary consequence of loosening of a specimen in the clamps and provides a useful criterion for suspecting this condition.

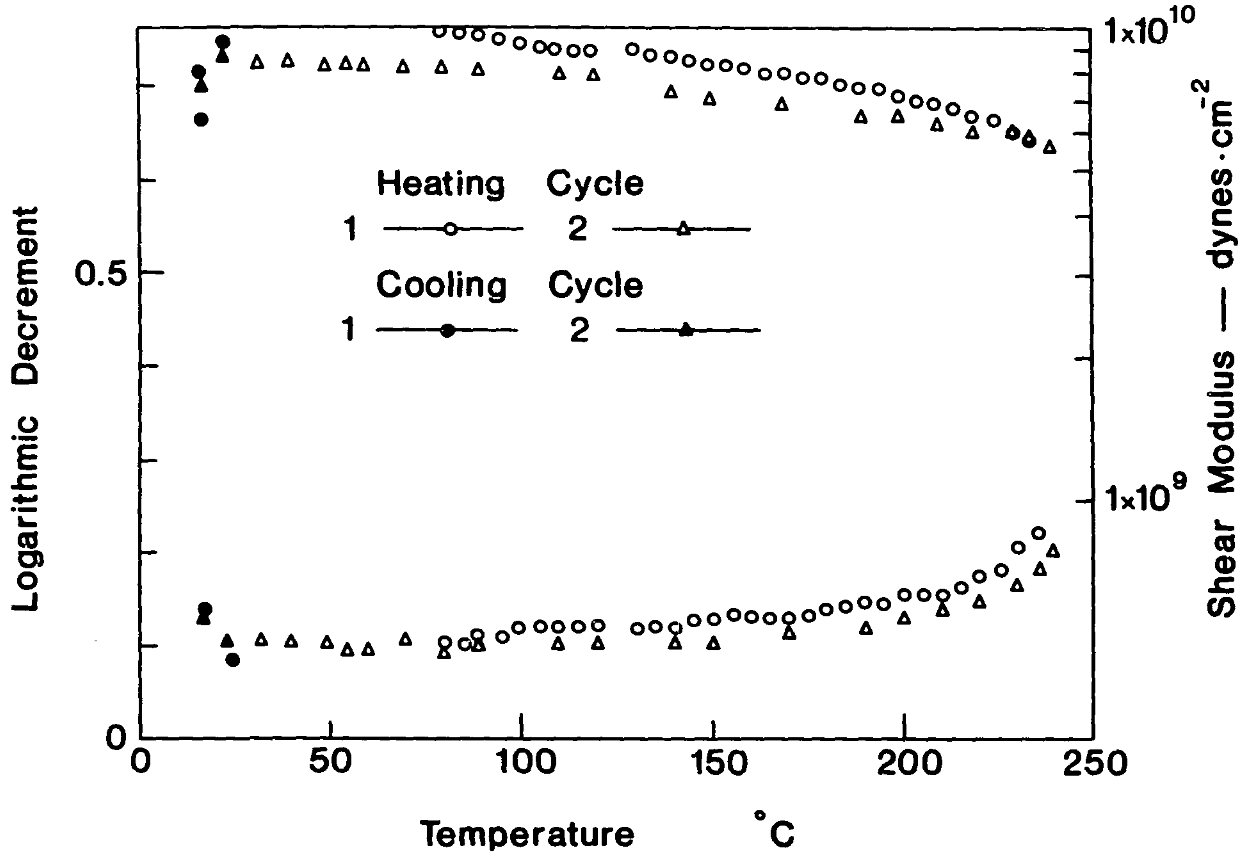

FIG. 12

Variation of elastic shear modulus and log decrement with temperature during two heating cycles for a dry, extracted spruce specimen. Thermally induced irreversible changes occur during the first heating cycle.

Since loosening of the specimen in the clamps caused concern, curves obtained during the heating cycle were scrutinised for variation of oscillation frequency. None was found and hence it was assumed that loosening occurred only during the cooling cycle.

After the clamps were retightened the shear modulus at room temperature was still lower than that obtained for the air-dry specimen indicating that thermally induced irreversible changes had occurred in the specimen.

The shear modulus decreased somewhat more slowly during the second heating cycle and finally attained a value of 5.7×10^9 dynes/cm^2 at 240°C, identical with that obtained at the end of the first heating cycle. On cooling to room temperature the clamps again loosened but after retightening the value of the modulus obtained was the same as that measured prior to the second heating cycle. These results suggest that all the thermally induced irreversible structural changes which affect the rigidity of the specimen occurred during the first heating cycle. To test this idea another spruce sample prepared in a similar manner was subjected to three heating cycles. The temperature dependence of the shear modulus is shown in Fig. 13. Although slightly lower values of the modulus were obtained throughout, the temperature dependence of the moduli for the two specimens was very similar and remained unchanged from the second to the third heating cycles. This confirmed the previous finding that all thermally induced change in the wood structure

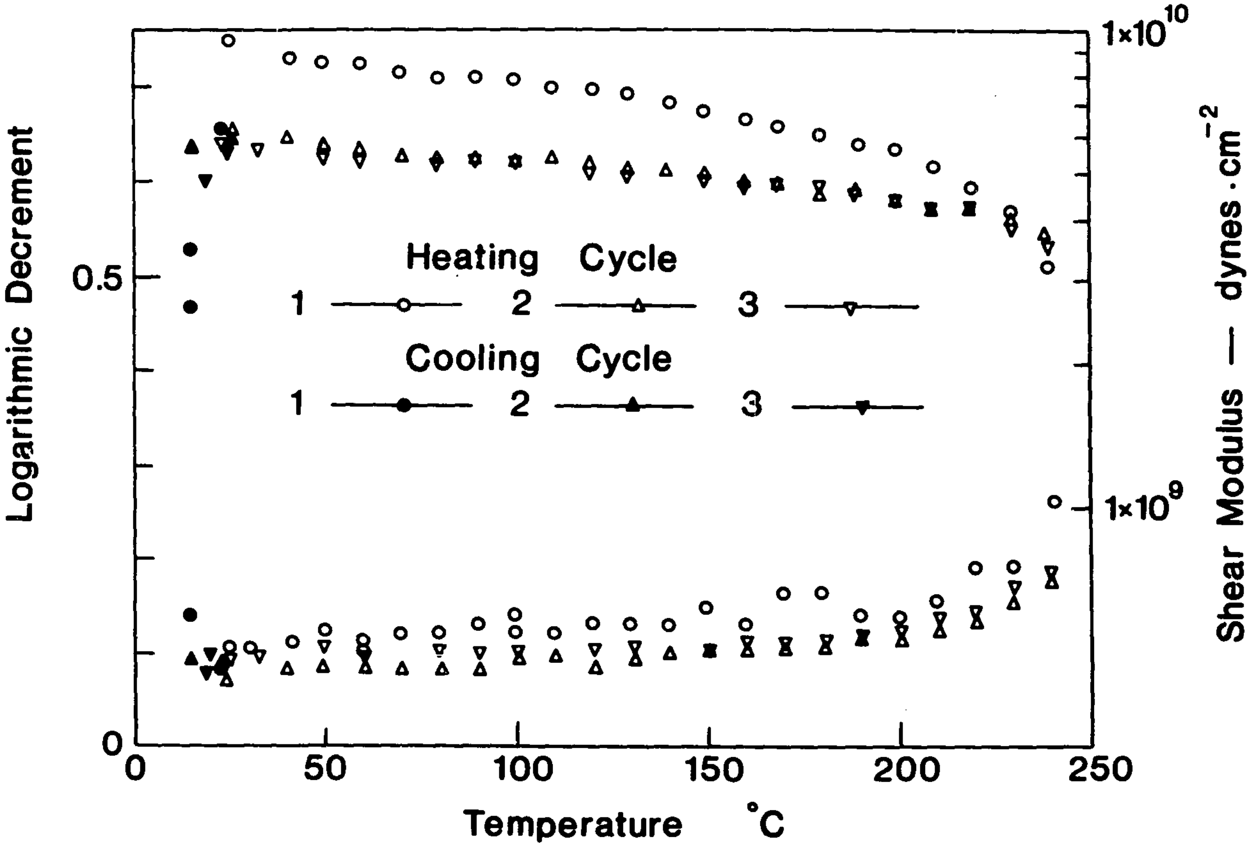

FIG. 13

Variation of elastic shear modulus and log decrement with temperature during three heating cycles for a dry, extracted spruce specimen. Curves obtained in the second and third cycles coincide, indicating that the temperature dependence of the mechanical properties is reversible after the first heating cycle. The more pronounced rate of change of the mechanical properties above 200°C indicates the onset of a transition.

occurred during the first heating cycle.

Variation of the log decrement with temperature for the two specimens seen in the respective figures shows a gradual increase up to 200°C followed by a slight upward swing between 200-240°C. This temperature dependence is compatible with that of the elastic shear modulus and indicates the onset of a transition in the range 200-240°C.

Similar results were obtained for birch and a typical set of data for three heating cycles is shown in Fig. 14. It will be noticed that for birch thermally induced changes continue to occur through the second heating cycle. There was also strong evidence for the onset of a glass transition in birch at 200°C as shown by the pronounced rise in log decrement and fall in shear modulus at that temperature. These changes are more abrupt than those occurring in spruce wood.

All specimens became quite dark during the first heating cycle and showed an increasing amount of surface charring with further exposure to high temperatures in subsequent heating cycles.

Results for both specimens are consistent with a small amount of thermally induced structural change. In addition to this there is reversible softening of the wood components and evidence for the onset of a glass transition in the region of 200-240°C. These results are in general agreement with those obtained by Goring and Baldwin (11) on powdered spruce and birch, which show a gradual softening up to 100°C followed by a sharp

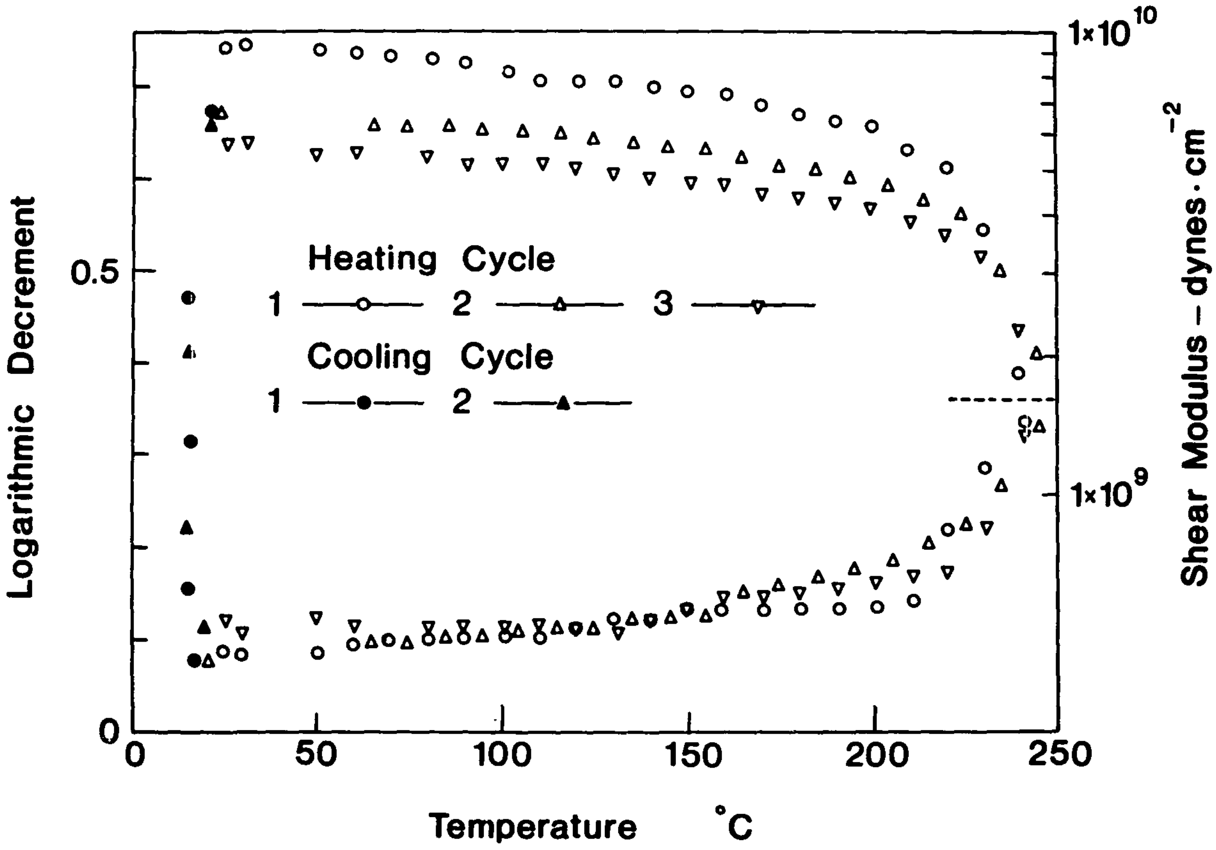

FIG. 14

Variation of elastic shear modulus and log decrement with temperature during three heating cycles for a dry, extracted birch specimen. The loss of rigidity during the second cycle is less than that in the initial cycle. Onset of a transition is indicated by the increase in the rate of change of the properties above 200°C. This increase is more pronounced than for the spruce specimens.

glass transition at 230°C.

2. In the Water-swollen State Through the Temperature Range 5-90°C

An extracted sample was prepared for testing in the water-swollen state by mounting it in the torsion pendulum and immersing overnight in the water thermostat at room temperature. In this manner the sample attained a moisture content of approximately 50% prior to testing.

Typical data showing the temperature dependence of elastic shear modulus and log decrement of extracted spruce and birch in water are seen in the curves on the extreme left of Figs. 15 and 16 respectively. Comparison of these data with those obtained previously for dry wood shows the marked effect of plasticization of both species by water. For water-plasticized wood the shear modulus is about half, and the log decrement is about double, that of a similar dry specimen at room temperature. These differences become more pronounced at higher temperatures. Both species exhibit an almost linear decrease of modulus up to 60°C, followed by a more rapid decrease up to 90°C. Log decrement increases through the temperature range 20-60°C, exhibits a small peak in the range 65-70°C, after which it shows a further increase up to 90°C.

Thus, two major differences between dry and wet wood are evident. The rigidity is lower and the mechanical damping

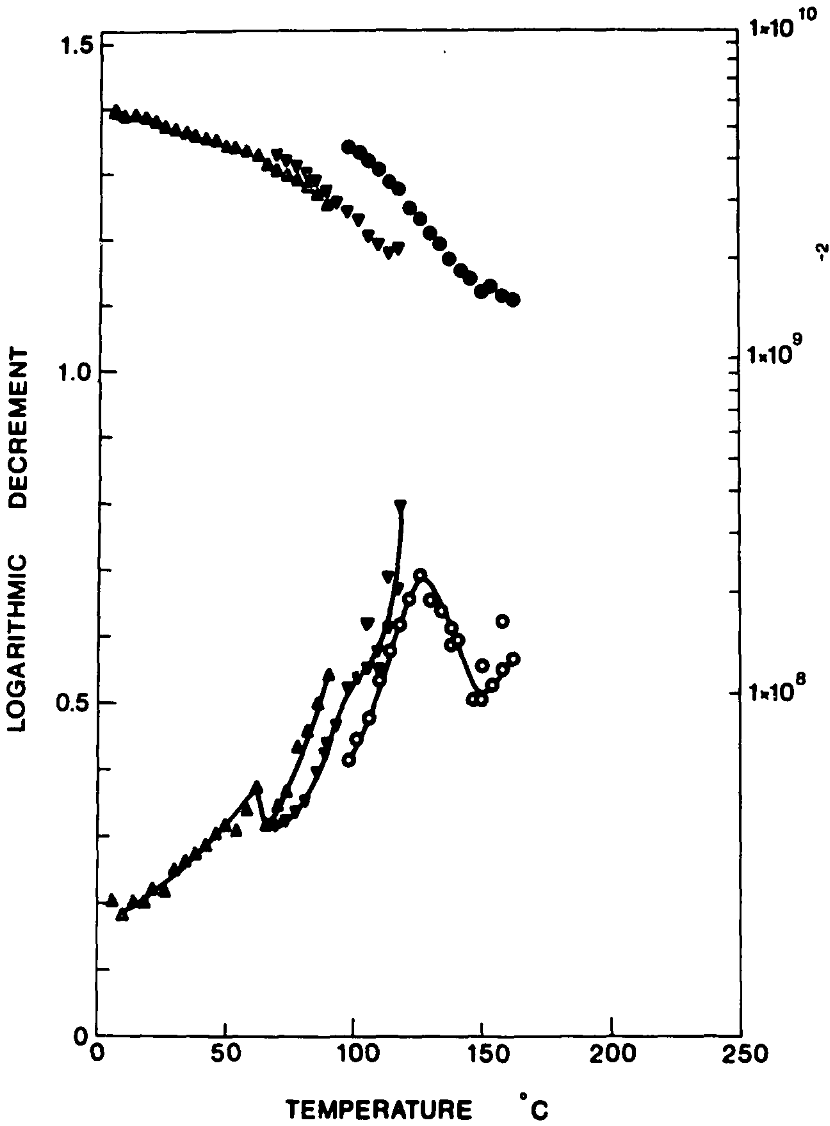

FIG. 15

Variation of elastic shear modulus and log decrement with temperature for an extracted spruce specimen swollen in water-△ -, in a water-glycerol mixture-▽ - and in glycerol-O-. A small transition in the range of 60-65°C in water and a large one in the range of 120-130°C in glycerol can be observed. Glycerol has a smaller plasticizing effect than water.

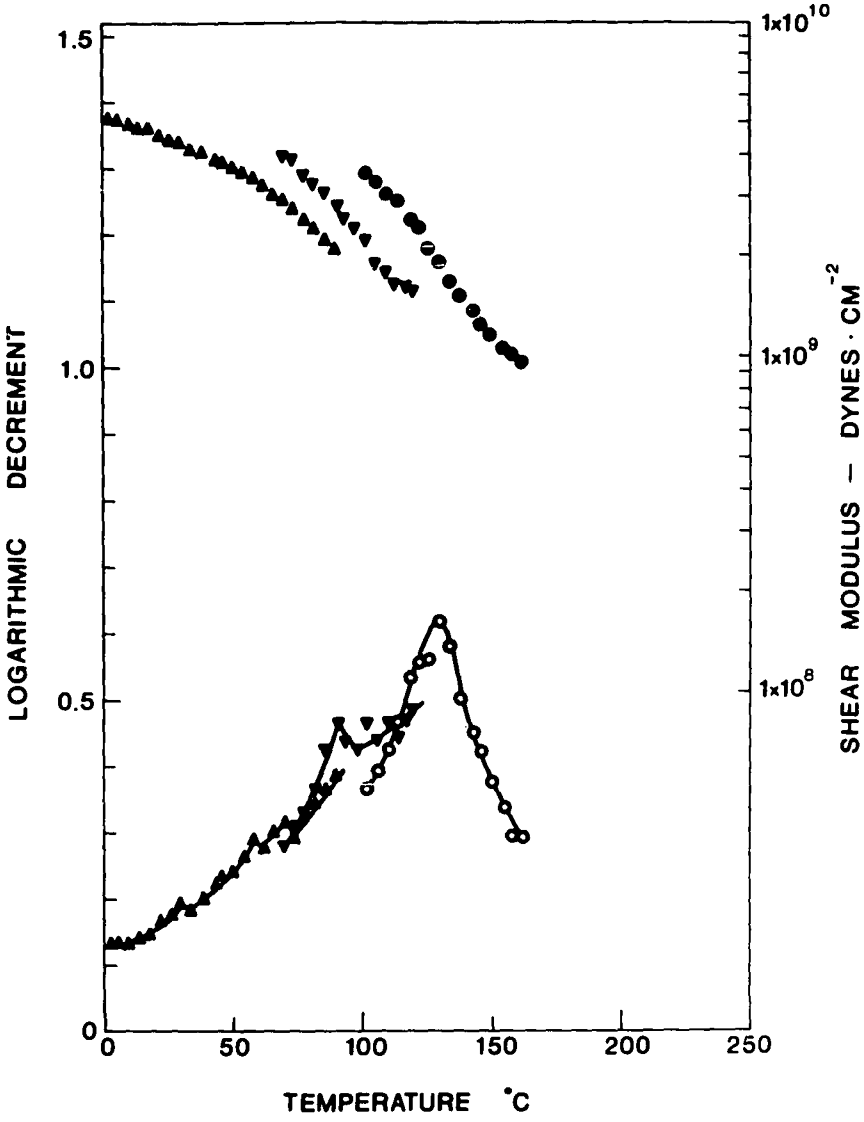

FIG. 16

Variation of elastic shear modulus and log decrement with temperature for an extracted birch specimen in water-Δ-, in a water-glycerol mixture-∇- and in glycerol-O-. Three small transitions in the range of 35-70°C in water and a large transition at approximately 130°C in glycerol can be observed. The shapes of the curves for birch are generally similar to those obtained for spruce.

is higher in wet wood. Furthermore, the rate of change of these properties with temperature is much greater in the wet condition through the temperature range 5-90°C. There is also evidence of a transition at about 65-70°C for both species in the moist condition and a hint of two additional transitions in birch at about 35-40°C and 55-60°C. It should be noted that the error in the measurements of both shear modulus and log decrement lies within the dimensions of the triangular markers used to plot the data. Consideration of Goring's findings (10) suggest that these transitions are due to thermal softening of hemicelluloses in the swollen wood structure. Whatever their origin the effect of these changes on the overall structure is quite small.

Comparison of Water and Glycerol as Plasticizers

Figs. 15 and 16 also show the effect of temperature on the same spruce and birch specimens tested to between 120-130°C in a 50-50 mixture of water and glycerol, and to 160°C in reagent-grade glycerol. Each specimen was tested in the three liquids in succession without disturbing its setting in the torsion pendulum. After each change of bath liquid at room temperature the sample was left submerged overnight and approached an equilibrium condition between the liquid and the specimen. It had been established previously that the dynamic mechanical properties being measured did not change much after standing for two hours in the liquid bath.

At a given temperature in the range where measurements were made in both liquids, values of the shear modulus for spruce and birch are higher in the water-glycerol mixture than in water. Similarly, they are higher in glycerol than in the mixture. The log decrement values are correspondingly lower. Thus, wood behaves as if it were dryer in glycerol than in water. This may be due to the fact that the smallest pores of the cell-wall structure can be penetrated by water molecules but not by larger glycerol molecules (29). Thus, glycerol molecules are not able to reach all the sites in the cell wall at which plasticization can occur.

The large peak in the log decrement curve and the corresponding inflexion in the shear modulus curve obtained in glycerol at approximately 130°C indicates a second-order transition. This will be discussed in more detail later. It will be noticed that the shapes of the curves obtained in the three liquids through the overlapping temperature range are quite similar. In fact, a transposition of the curve obtained in glycerol through 10-15°C would allow it to be superimposed on the curve obtained in the water-glycerol mixture. A similar transposition could be made between the curves obtained in the mixture and water respectively. Finally, it is observed that the curves obtained in the mixture generally lie between those obtained in water and glycerol respectively. The only exception to this is in the log decrement curve for birch through the region 80-90°C.

3. Effect of Pre-steaming at 180°C for Three Minutes

Wood chips are often mechanically processed after steaming under pressure at 180°C for about 3 minutes (11,16). To determine whether such treatment causes any permanent change in structure which can be detected by change of its dynamic mechanical properties, two typical extracted black spruce specimens were steamed under these conditions prior to testing. Each specimen was tested in all three liquids according to the procedures described in the previous section. Results are given in Figs. 17 and 18.

Values of the elastic shear modulus for both steamed specimens are considerably lower than that obtained for the typical unsteamed specimen at room temperature as shown in Fig. 15. This difference is maintained throughout the temperature range 5-90°C, showing that the pre-steaming has permanently softened the wood. The change of shear modulus with temperature is slightly less for the steamed specimens. Corresponding values of the log decrement are also lower for the steamed specimens. Thus, steaming alters the wood structure in such a way as to make it more rubbery, i.e. more elastic and less rigid. These structural changes may be associated with permanent flow of hemicelluloses.

In order to study the relative effect of the three plasticizers, tests similar to those described in the preceding section were conducted. There appears to be little difference between the effect of water and that of the water-glycerol

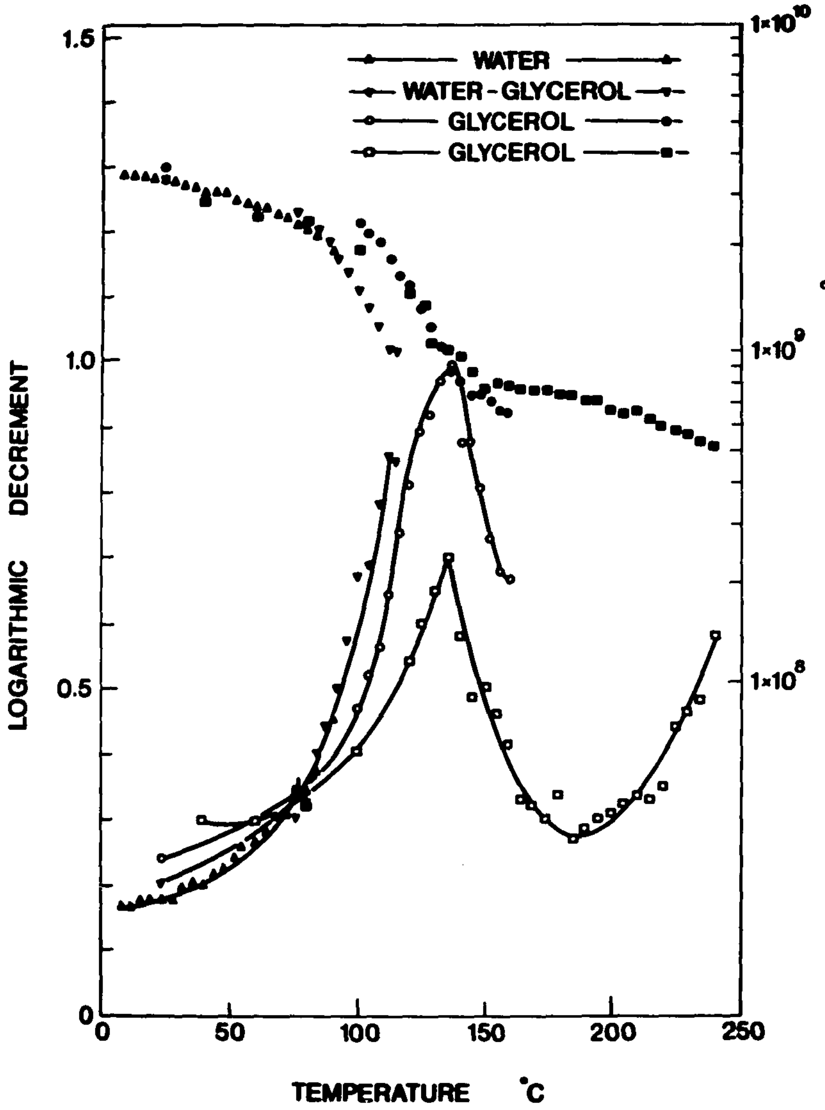

FIG. 17

Variation of elastic shear modulus and log decrement with temperature for an extracted, pre-steamed spruce specimen in three plasticizing liquids. Shear modulus and log decrement are lower than for untreated specimen indicating that the wood behaves as if it is softer but more elastic after steaming. The difference between water and water-glycerol curves is very small. Curves of the two heating cycles in glycerol are of similar shape and a transition can be observed at approximately 135°C on each of these curves.

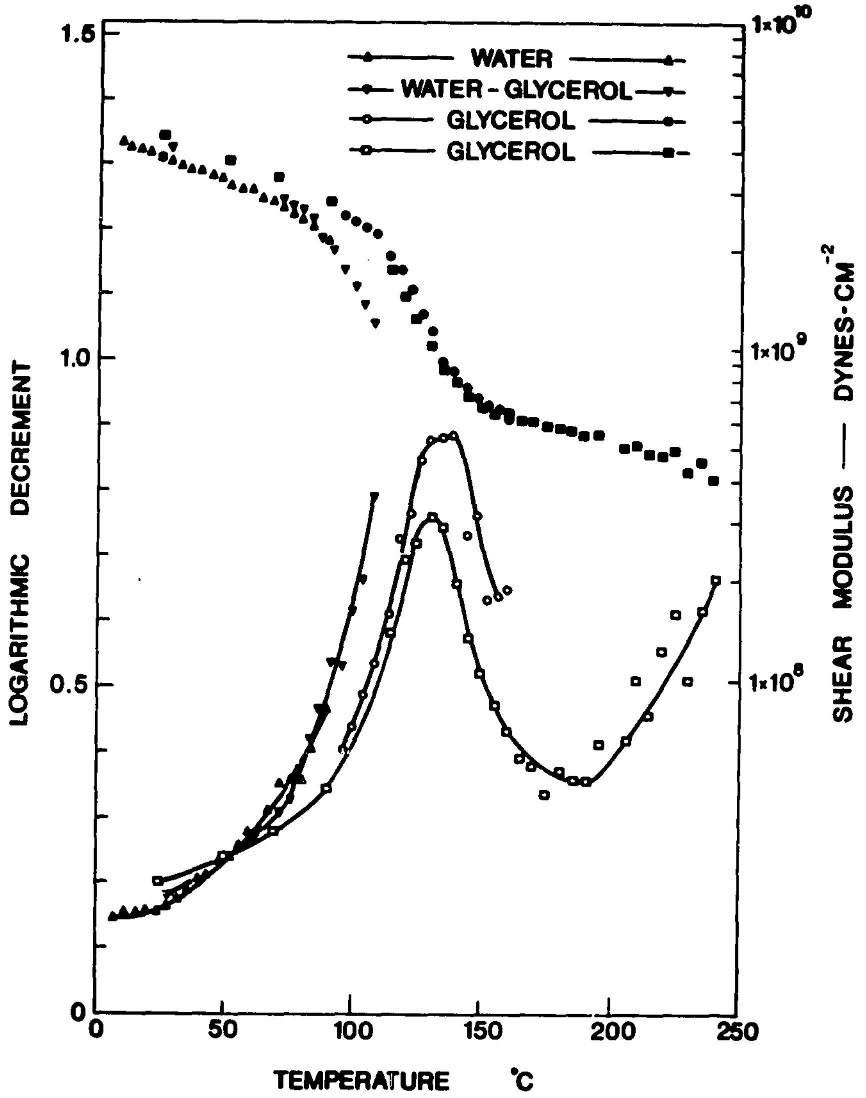

FIG. 18

Variation of elastic shear modulus and log decrement with temperature for an extracted pre-steamed spruce specimen in plasticizing liquids. The curves are very similar to those of Fig. 17 which were obtained on an identical series of tests showing the good reproduciblity of the experimental technique.

mixture since the curves for steamed spruce in the mixture were found to be almost a continuation of those obtained in water. In glycerol the curves are transposed by about 10-15°C to higher temperatures, and although the value of the peak in the log decrement curve is somewhat higher for the steamed than for the unsteamed specimen, there is no change in the transition temperature.

Two series of tests were conducted in glycerol. The first series was conducted in the open laboratory and since intense noxious fumes were emitted from the glycerol bath it became physically impossible to continue the test above 160°C. The specimens were removed from the apparatus and stored in a refrigerator for two months prior to retesting through the temperature range 20-240°C in a fume hood. Data obtained in the two series of tests are shown in Figs. 17 and 18. The only noticeable difference between the results of the two test series is in the peak values of the log decrement, which are significantly lower after standing in glycerol for a period of two months. This drop may be due to the slow removal of small remaining traces of water during the two-month period of standing. If such were the case, one might also expect a change in the shear modulus yet no such change is apparent. Despite this drop in the values of the log decrement, in both instances the transition temperature remains unchanged.

Finally, it should be noted that there was no discoloration of the specimens during the tests in both water and the water-glycerol mixture. The specimen darkened slightly during the first test in glycerol up to 160°C and became very dark after the second test in which it was exposed to a temperature of 240°C.

Fig. 19 shows typical data obtained for an extracted birch specimen which was pre-steamed in a manner similar to that for spruce. Comparing these results with those obtained for the unsteamed specimen shown in Fig. 16, it is seen that there is little change in the temperature dependence of the shear modulus. Unlike spruce, however, birch shows a higher log decrement in water after the pre-steaming treatment and the transitions become more pronounced. In glycerol there is very little change on pre-steaming.

4 and 5. Extracted and Pre-steamed in Glycerol Through Temperature Range 20-240°C

Fig. 20 shows the temperature dependence of the dynamic mechanical properties for an extracted black spruce specimen which was submerged in glycerol overnight prior to testing. There is an inflexion in the shear modulus-temperature curve in the temperature range 105-145°C and the modulus decreases from 3.5×10^9 to 1.5×10^9 dynes/cm^2 through this range. The log decrement-temperature curve exhibits a peak value of 0.66 at approximately 130°C. It may be concluded that untreated spruce undergoes a second-order transition at

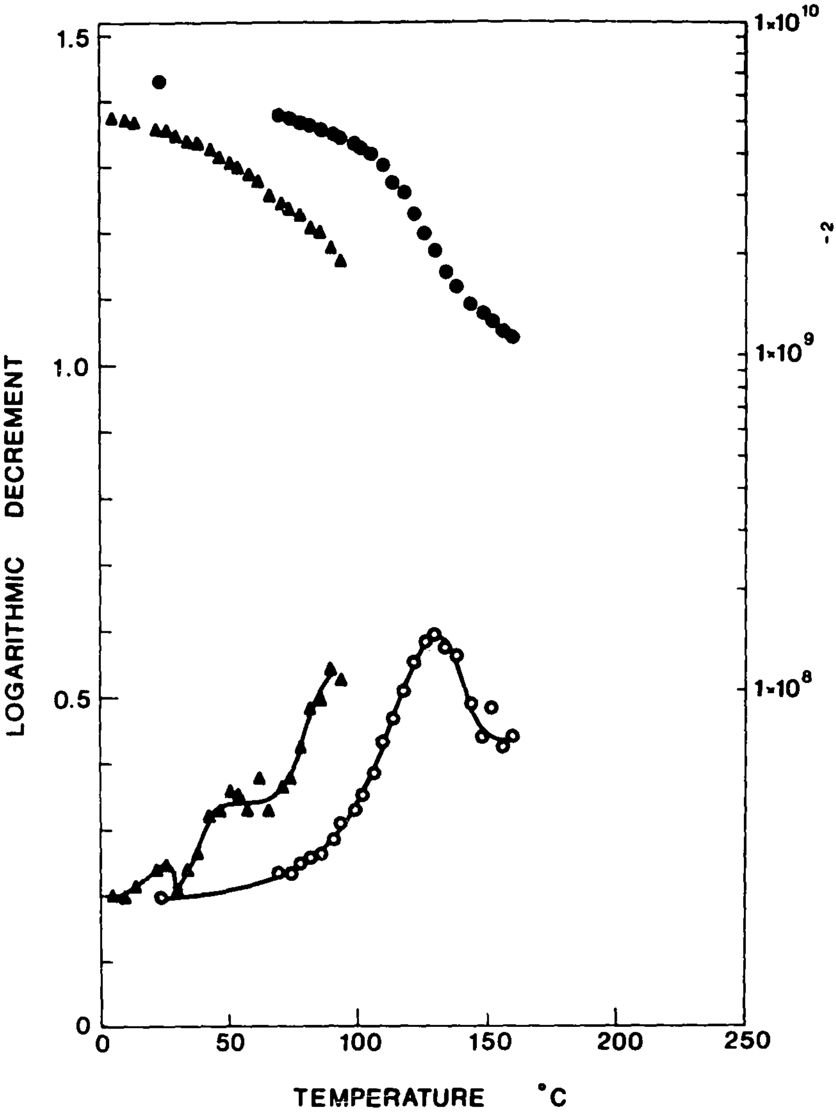

FIG. 19

Variation of elastic shear modulus and log decrement with temperature for an extracted pre-steamed birch specimen in water and glycerol. With the exception of the log decrement curve in water which shows an upward shift and two distinct small transitions, there is almost no difference between the above curves and those obtained for the untreated birch specimen.

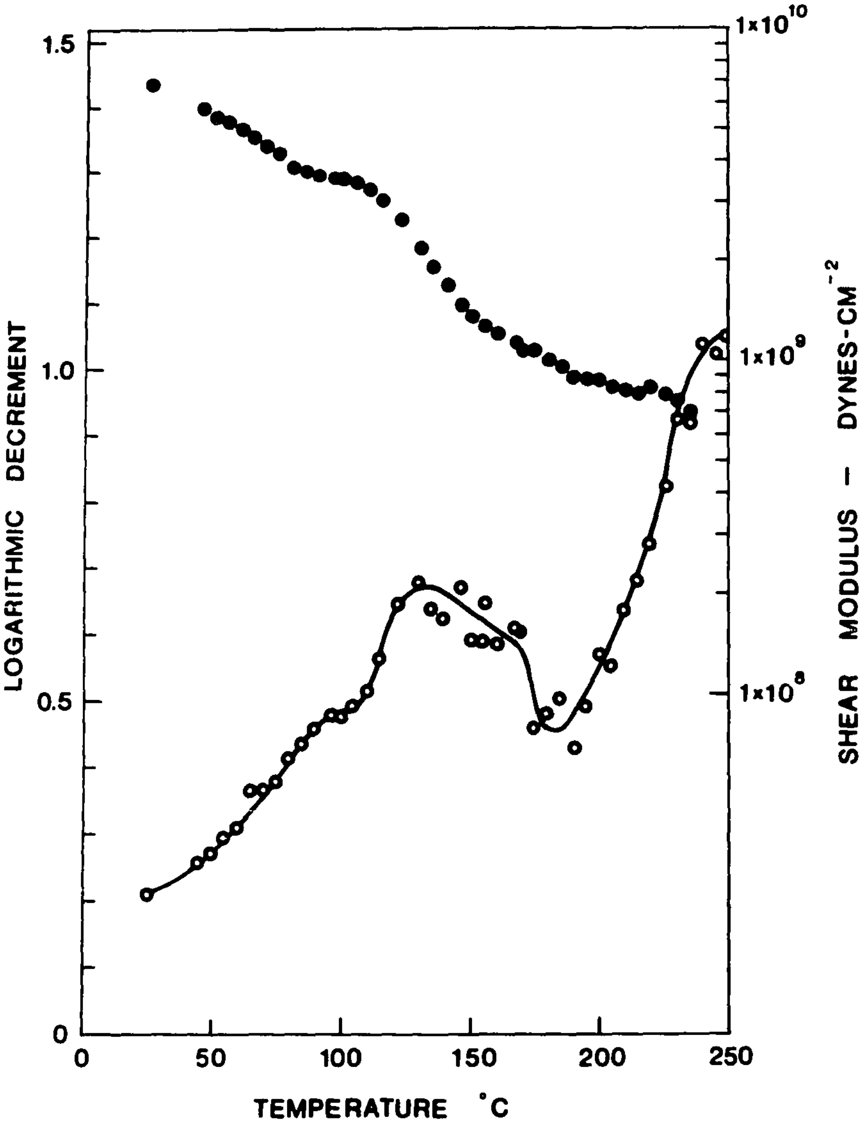

FIG. 20

Variation of elastic shear modulus and log decrement with temperature for an extracted spruce specimen in glycerol. A large transition at approximately 130°C and two smaller ones at 100°C and 65°C can be seen.

approximately 130°C for low frequency torsional oscillation. Small transitions at approximately 65°C and 100°C may also be seen. The reduction in shear modulus through the major transition is not of the same magnitude as that observed for a synthetic polymer (see Fig. 3). This is not surprising when one considers that wood is a polymer-composite and it is highly likely that thermal softening of only one component is taking place at 130°C.

Similar tests for a birch specimen exhibited a transition at approximately 130°C as shown in Fig. 21. The peak in the log decrement-temperature curve is well defined in contrast to the broad curve obtained for spruce. There is no evidence of any low temperature transition in untreated birch. It was not possible to measure the high damping values beyond 215°C with the present apparatus, but the shape of the curves would tend to suggest a larger transition exists above this temperature.

There is evidence (11) to indicate that the transition at approximately 130°C is due to softening of lignin in both species.

As previously indicated, it is of interest to study the effect of pre-steaming on the mechanical properties of these species. The effect of pre-steaming extracted spruce at 180°C for 3 minutes is shown in Fig. 22. There is a small reduction in the transition temperature and the log decrement curve is smoother and sharper than that for the untreated

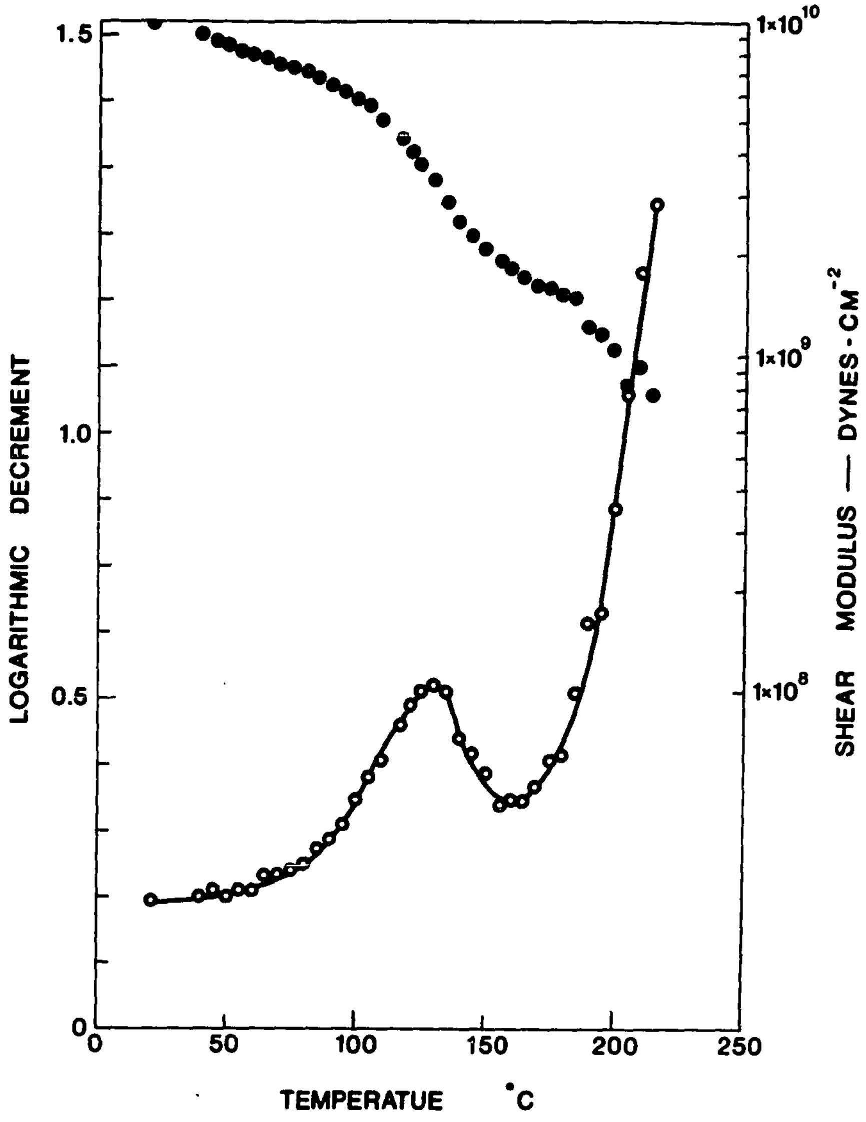

FIG. 21

Variation of elastic shear modulus and log decrement with temperature for an extracted birch specimen in glycerol. A sharp transition at 130°C can be observed. The shear modulus is higher and the log decrement is lower than for spruce up to the abrupt increase of slope at approximately 180°C.

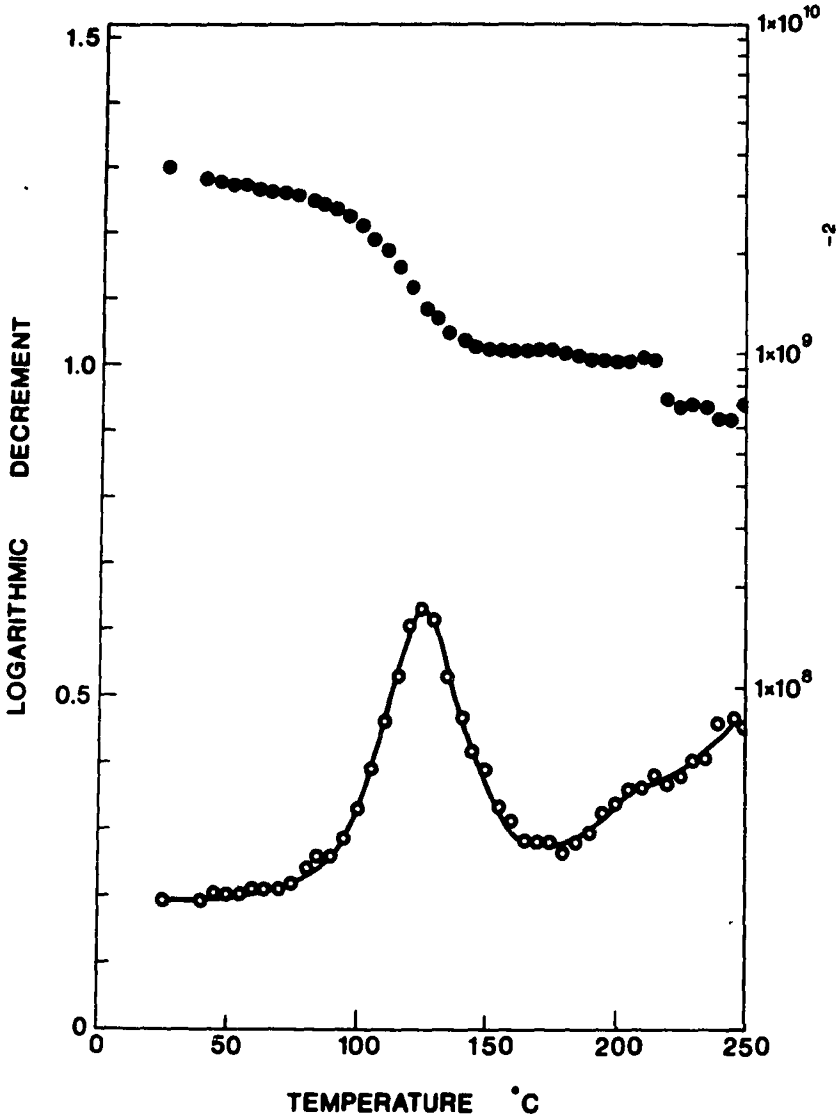

FIG. 22

Variation of elastic shear modulus and log decrement with temperature for an extracted, pre-steamed spruce specimen in glycerol. Compared with the unsteamed spruce specimen there is little change in the transition temperature, but the small transitions are not seen. The values of shear modulus and log decrement are lower than for the unsteamed specimen.

specimen. The low temperature transitions have disappeared and the values of log decrement are lower above and below the transition temperature. These changes may be associated with the flow of hemicelluloses during the steaming process. There is a decrease in shear modulus at the lower temperatures indicating that the spruce specimen has been softened by the steam treatment.

The effects which accompany the pre-steaming of birch are somewhat different as seen in Fig. 23. There is very little reduction of rigidity at any temperature due to steaming. The log decrement values are higher for the pre-stemaed specimen and the curve shows evidence of twin peaks at 130°C and 150°C.

6. Progressively Delignified Specimens in Glycerol Through Temperature Range 20-165°C

Extracted spruce and birch specimens were progressively delignified to yields shown in Table I by cooking in aqueous buffered sodium chlorite solutions at 50°C.

Fig. 24 shows the variation in elastic shear modulus and log decrement with temperature for a black spruce specimen from which approximately 1% of lignin had been removed. This small amount of delignification brings about a reduction of the transition temperature from 130°C to 100°C. The log decrement values increase and the shear modulus is reduced when the lignin is removed. There is a sharp increase in log decrement and a

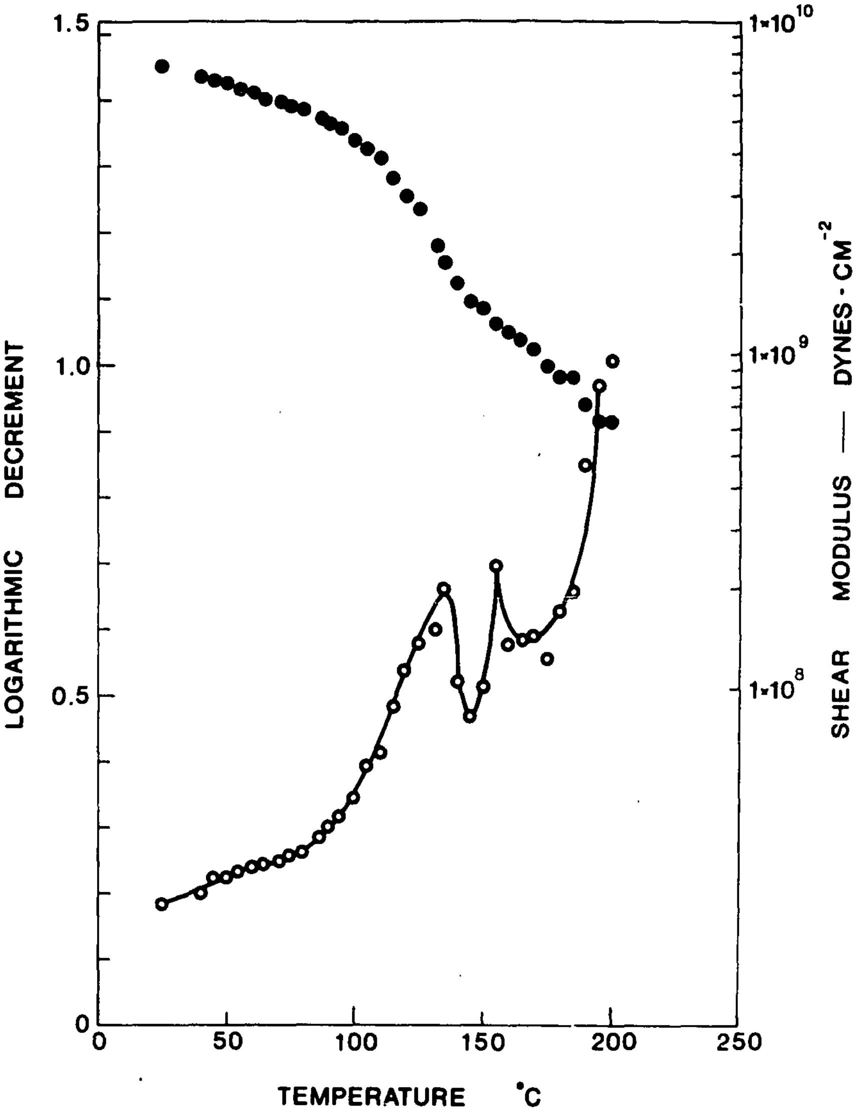

FIG. 23

Variation of elastic shear modulus and log decrement with temperature for an extracted, pre-steamed birch specimen in glycerol. The log decrement curve has a complex behaviour in the region of the transition. Compared to unsteamed birch the value of the shear modulus is lower and that of the log decrement is higher, but the shape of the curves is similar.

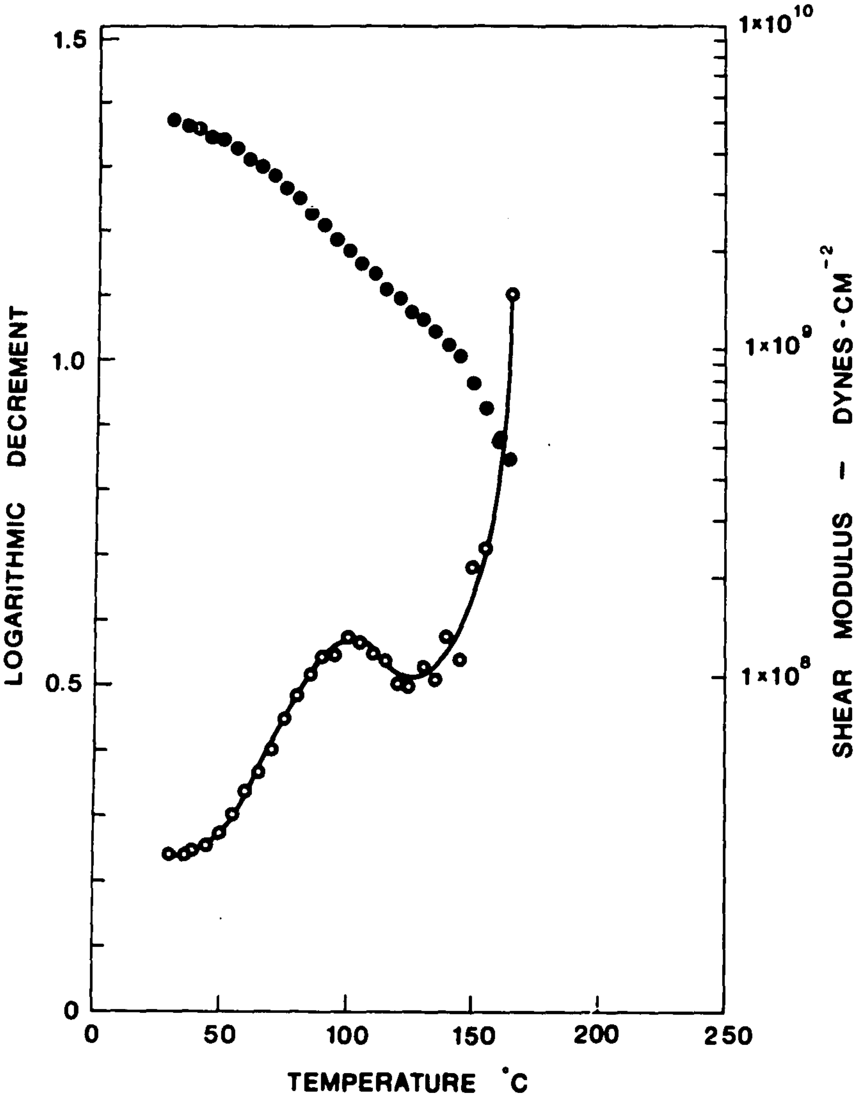

FIG. 24

Variation of dynamic mechanical properties with temperature for a partially delignified spruce specimen of 99.7% yield, in glycerol. As a result of delignification the rigidity of the specimen is noticeably decreased and the transition temperature is lowered by about 30°, to approximately 100°C. There is an abrupt softening above 150°C.

corresponding decrease in shear modulus curves at 150°C. It was not possible to make measurements above 165°C owing to the very high damping exhibited by the partially delignified specimen above this temperature. However, it is evident that the wood undergoes a major structural change above 150°C.

Further delignification caused the transition to shift to progressively lower temperatures. This may be seen in Fig. 25 for a sample from which approximately 36% of lignin has been removed and in Fig. 26, where approximately 58% lignin has been removed. The transition temperatures for these partially delignified specimens are approximately 70°C and 40°C respectively. As might be expected the spruce specimens become much less rigid, compatible with loosening of the wood structure by progressive delignification. This is seen by the upward shift in the log decrement-temperature curves and the corresponding downward shift of the shear modulus-temperature curves with increasing delignification. This trend continues with further delignification as seen in Fig. 27 which shows data obtained for a specimen with 68% of the lignin removed. There is no well defined transition temperature for this specimen.

A spruce specimen was cooked to 67% yield and presumably all the lignin and some of the hemicelluloses were removed. Even at room temperature this specimen had a log decrement above 1.20 and it was not possible to measure the damping values accurately as the temperature was raised.

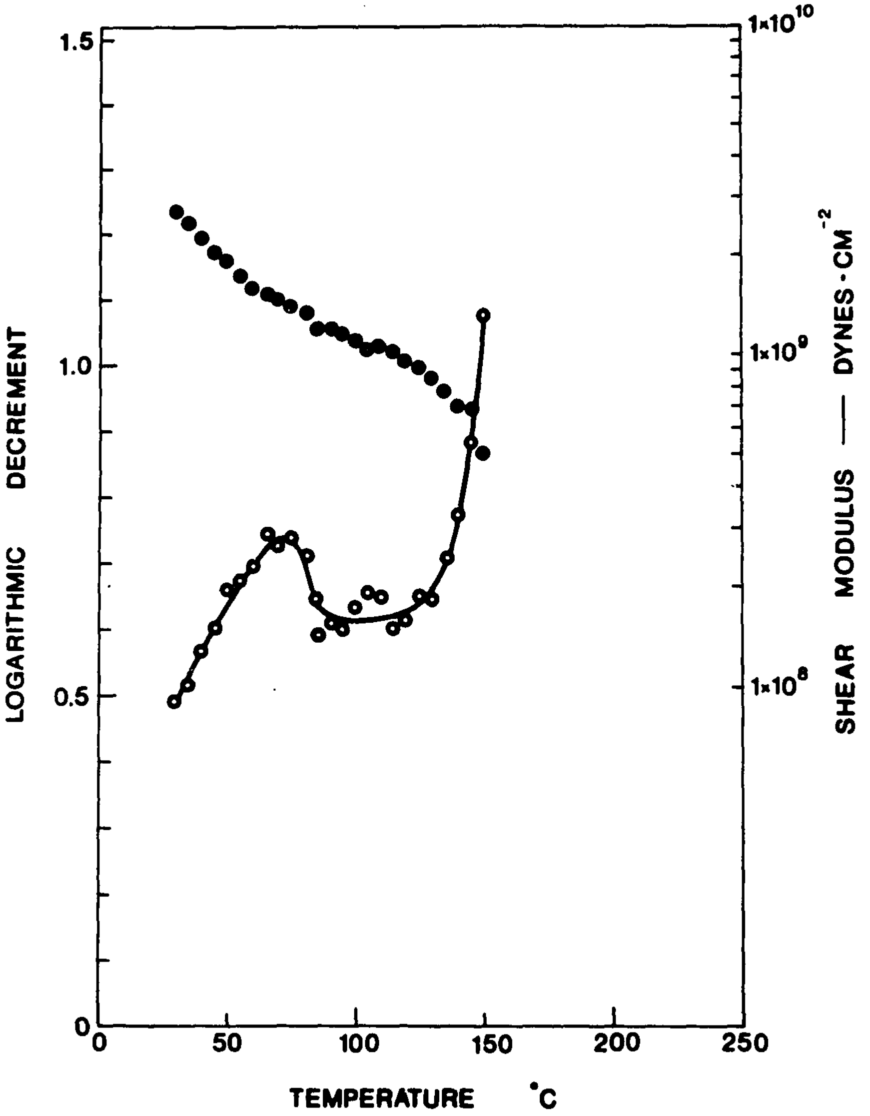

FIG. 26

Variation of dynamic mechanical properties with temperature for a partially delignified spruce specimen of 90.2% yield, in glycerol. The increase of log decrement and the corresponding decrease of shear modulus shows that spruce softens considerably with progressive delignification. The transition temperature has dropped to about 70°C.

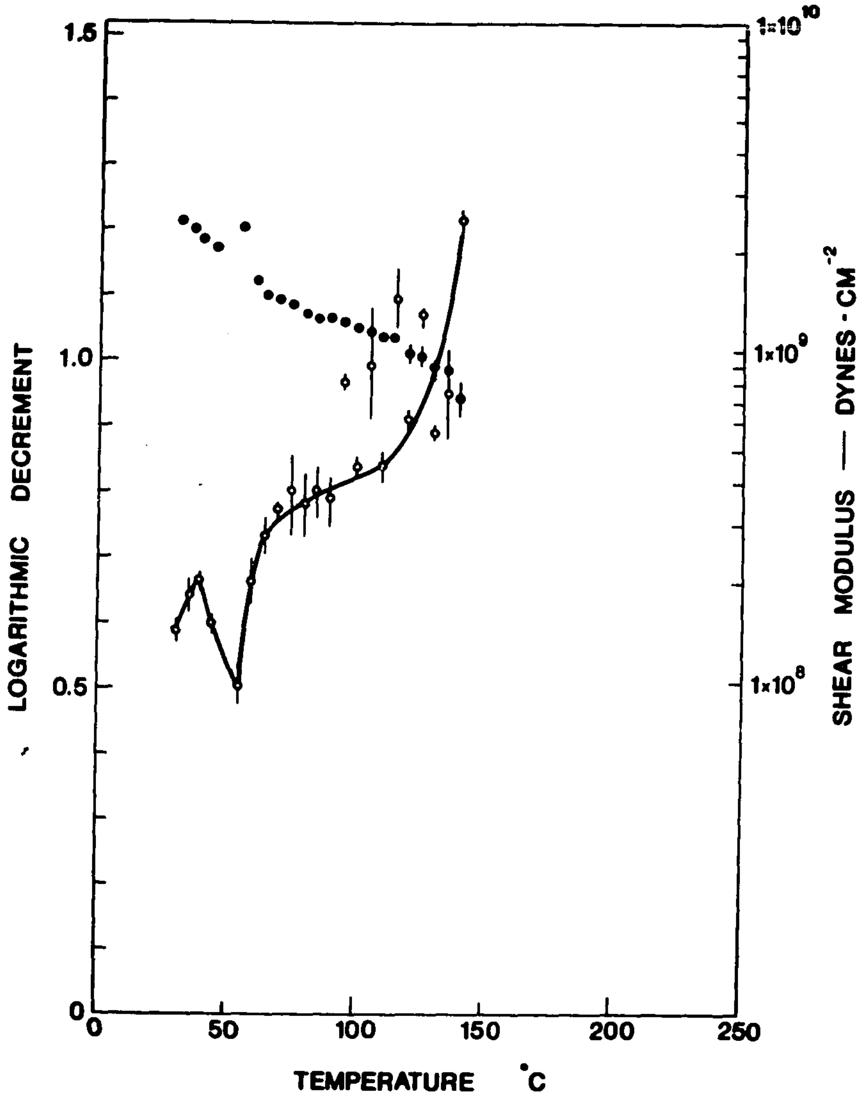

FIG. 26

Variation of dynamic mechanical properties with temperature for a partially delignified spruce specimen of 83.8% yield, in glycerol. A transition temperature in the range 40-50°C is seen. The peak in the log decrement curve is quite small. The vertical lines indicate the spread in the experimental values.

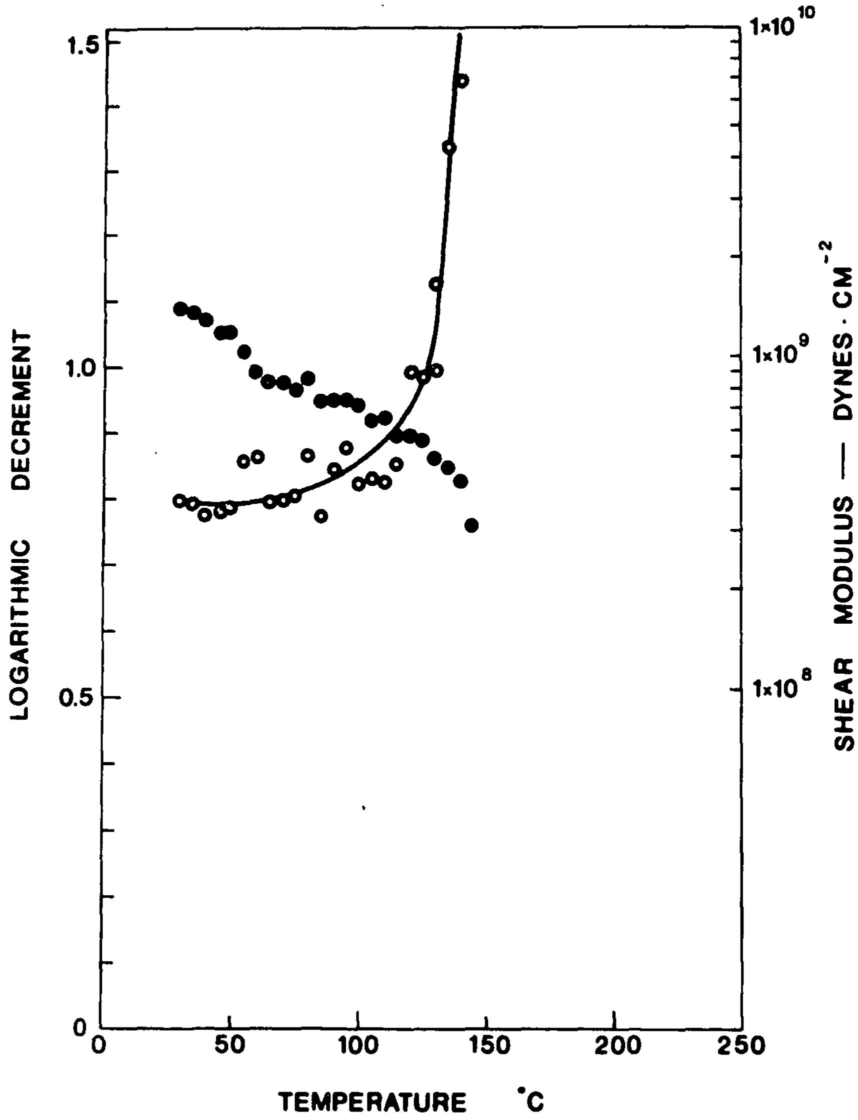

FIG. 27

Variation of dynamic mechanical properties with temperature for a partially delignffied spruce specimen of 81.0% yield, in glycerol. From the high value of the log decrement and correspondingly low value of shear modulus, it is evident that the wood has become quite soft and is about to undergo further softening at 150°C. It is not possible to detect any well defined transition.

It may be noted that the almost asymptotic rise at the right-hand side of the log decrement curves for spruce shifts to lower temperatures as the lignin content is decreased.

The effect of progressive delignification on the mechanical properties of birch is seen in Figs. 28-32. Unlike the situation for spruce, described above, it is not possible to detect an unambiguous trend in the curves for birch with decreasing lignin content. The transition temperature decreases to approximately 100°C for a specimen with 23% of its lignin removed as seen in Fig. 28. However, no transitions can be detected for specimens with 38 and 53% of the lignin removed as seen in Figs. 29 and 30 respectively. The specimen which has the most lignin removed (64%) shows a transition at approximately 65°C as seen in Fig. 32, and one with only 60% lignin removed shows two transitions at approximately 50°C and 115°C as seen in Fig. 31.

The values of shear modulus of all delignified specimens are lower than for the uncooked specimen. However, the decrease in modulus for birch which is brought about by delignification is not nearly as large as for spruce. In fact, with the exception of the specimen which has 60% lignin removed, the shear modulus-temperature curves of all other delignified specimens are almost identical. The log decrement-temperature curves for the delignified specimens are also identical over certain parts of the temperature range. In

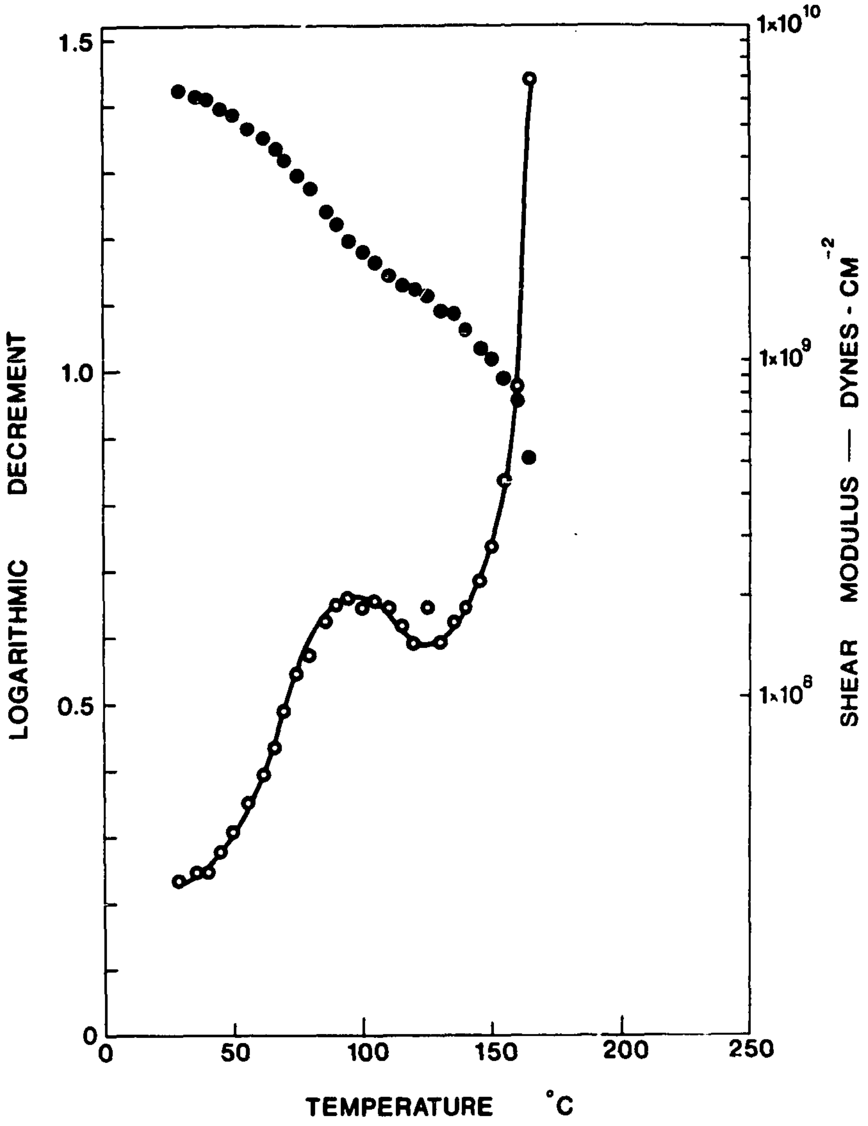

FIG. 28

Variation of dynamic mechanical properties with temperature for a partially delignified birch specimen of 95.6% yield, in glycerol. Compared to an untreated specimen this one is less rigid and transition temperature is lowered by about 30°C. All delignified birch specimens show an abrupt change in mechanical properties in the range 150-160°C.

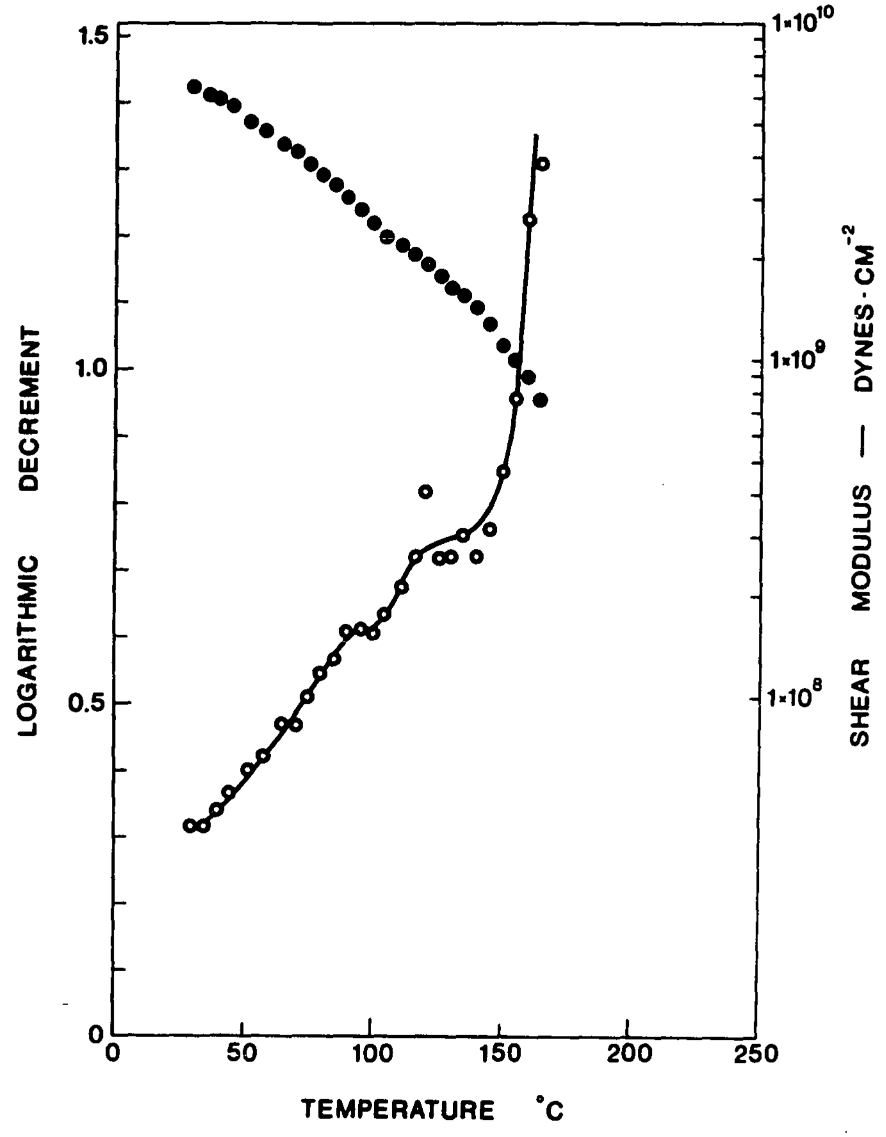

FIG. 29

Variation of dynamic mechanical properties with temperature for a partially delignified birch specimen of 92.7% yield, in glycerol. There is almost no change in the shear modulus curve when compared to Fig. 28. The log decrement shows an increase. No unambiguous transition temperature can be identified.

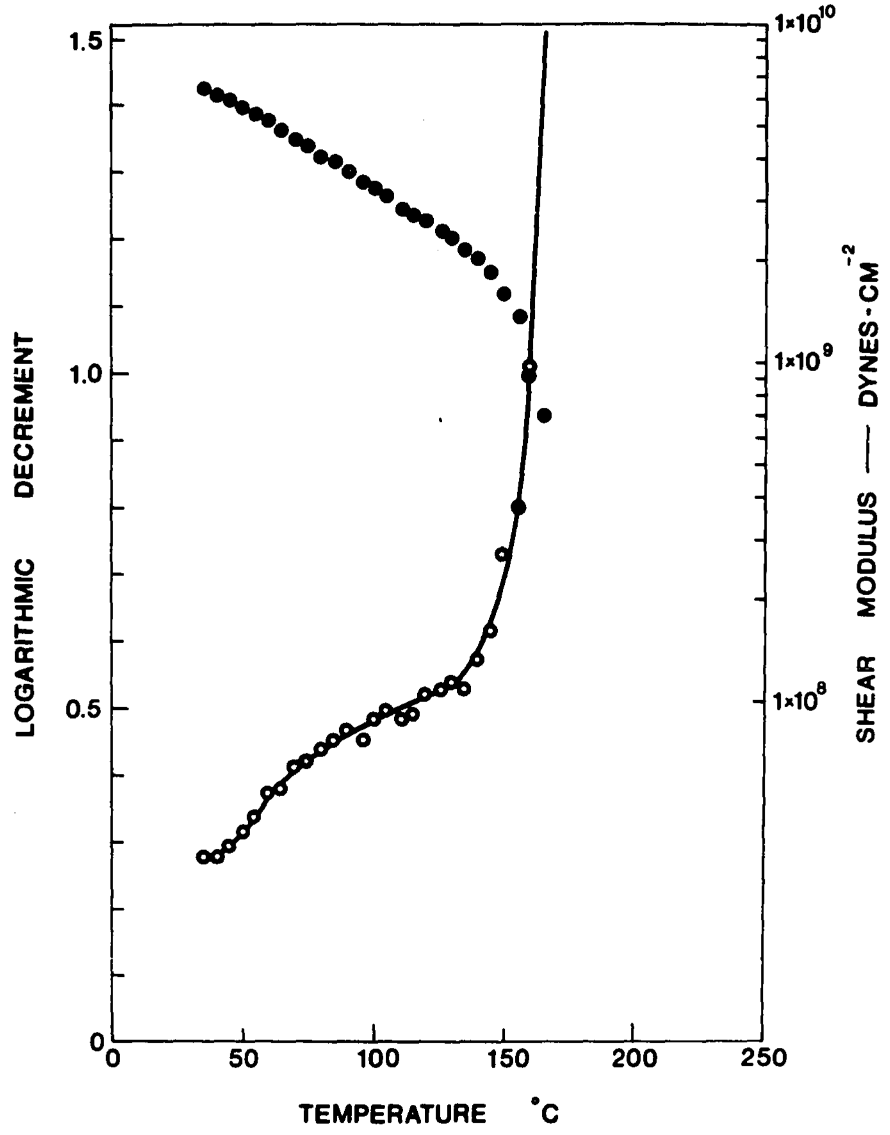

FIG. 30

Variation of dynamic mechanical properties with temperature for a partially delignified birch specimen of 90.0% yield, in glycerol. This specimen shows little change from the last one.

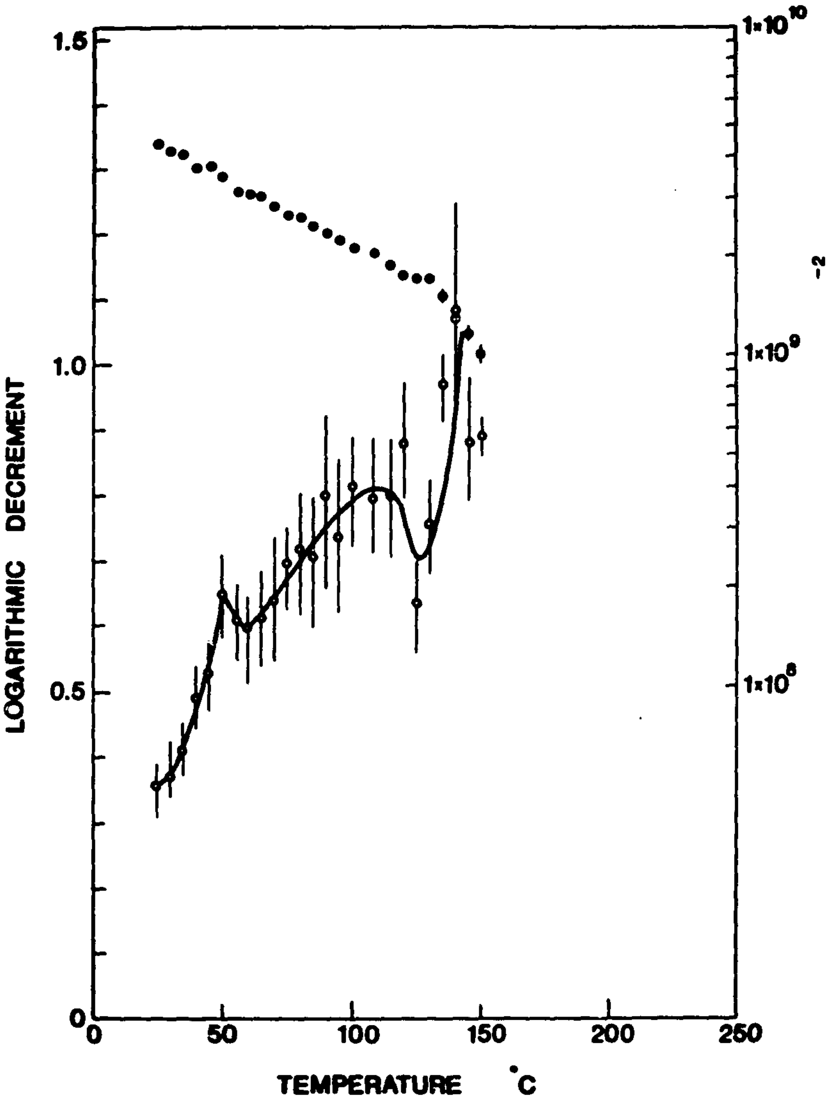

FIG. 31

Variation of dynamic mechanical properties with temperature for a partially delignified birch specimen of 88.6% yield, in glycerol. The specimen is softer than any of the previous birch specimens. Two small transitions in the range 45-55°C and 105-120°C can be seen. Vertical lines indicate the spread in the experimental data.

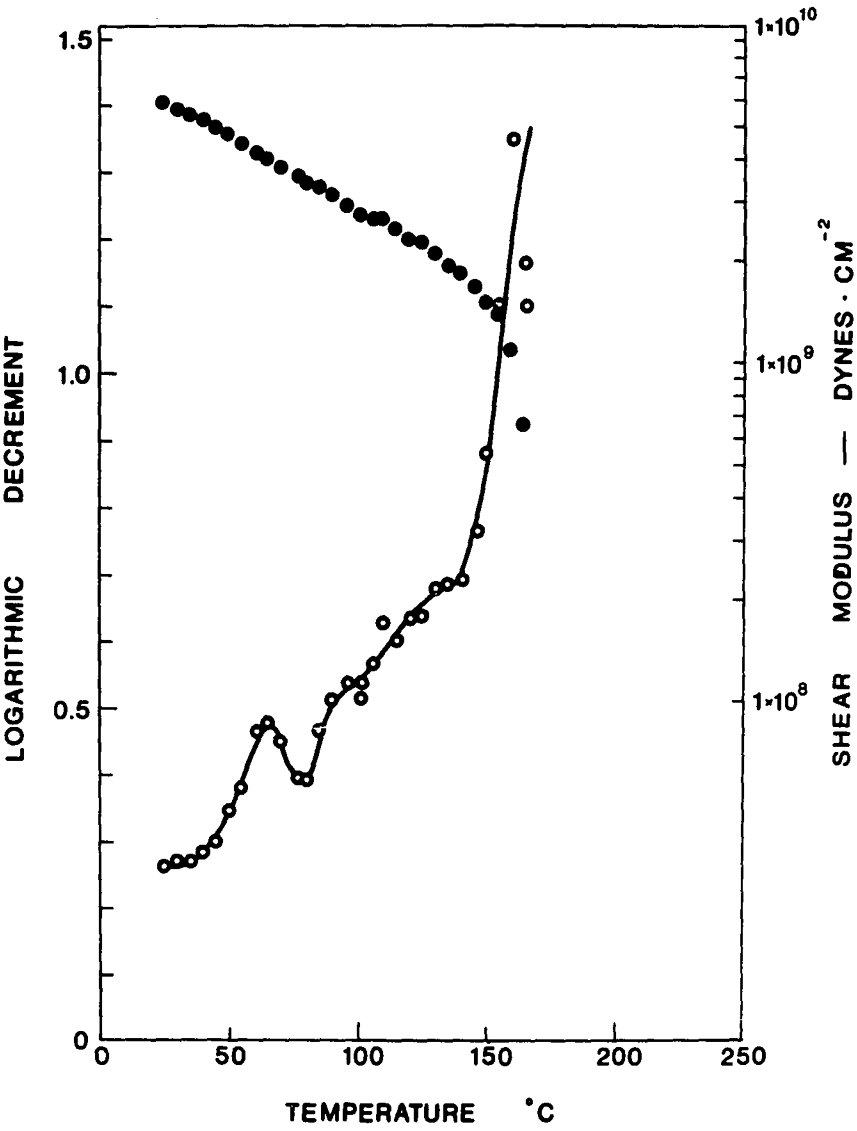

FIG. 32

Variation of dynamic mechanical properties with temperature for a partially delignified birch specimen of 87.9% yield, in glycerol. The specimen although delignified to a greater extent shows more stiffness than the last one. A transition in the range 65-75°C can be seen.

general, the curves are more complex than those for spruce.

The log decrement curves rise sharply at approximately 150°C for all partially delignified specimens, indicating a very extensive loss of rigidity above this temperature.

7. Time Dependence of the Mechanical Properties of Untreated Spruce in Glycerol Through the Temperature Range 20-240°C

Figs. 33a, b and c show the effect of successive cyclic heating and cooling to maximum temperatures of 100°, 130°, 175° and 240°C respectively on the mechanical properties of extracted spruce, in glycerol. 100°C was chosen as a convenient temperature below the transition temperature, 130°C, of untreated spruce; 175°C was chosen because it is the approximate temperature of the minimum in the log decrement-temperature curve above the transition.

Fig. 33a shows the results of the first two cycles. The temperature dependence of the mechanical properties appears to be completely reversible during the heating-cooling cycle up to 100°C. Values of the log decrement below 50°C in the cooling cycle are artificially high owing to a slight loosening of the clamps below this temperature. When the clamps were retightened prior to the second heating cycle, there was a drop of about 0.05 in the value of the log decrement at room temperature. Results obtained during the second heating cycle up to 100°C were coincident with those obtained during the first heating cycle. There appears to be a transition at 120°C.

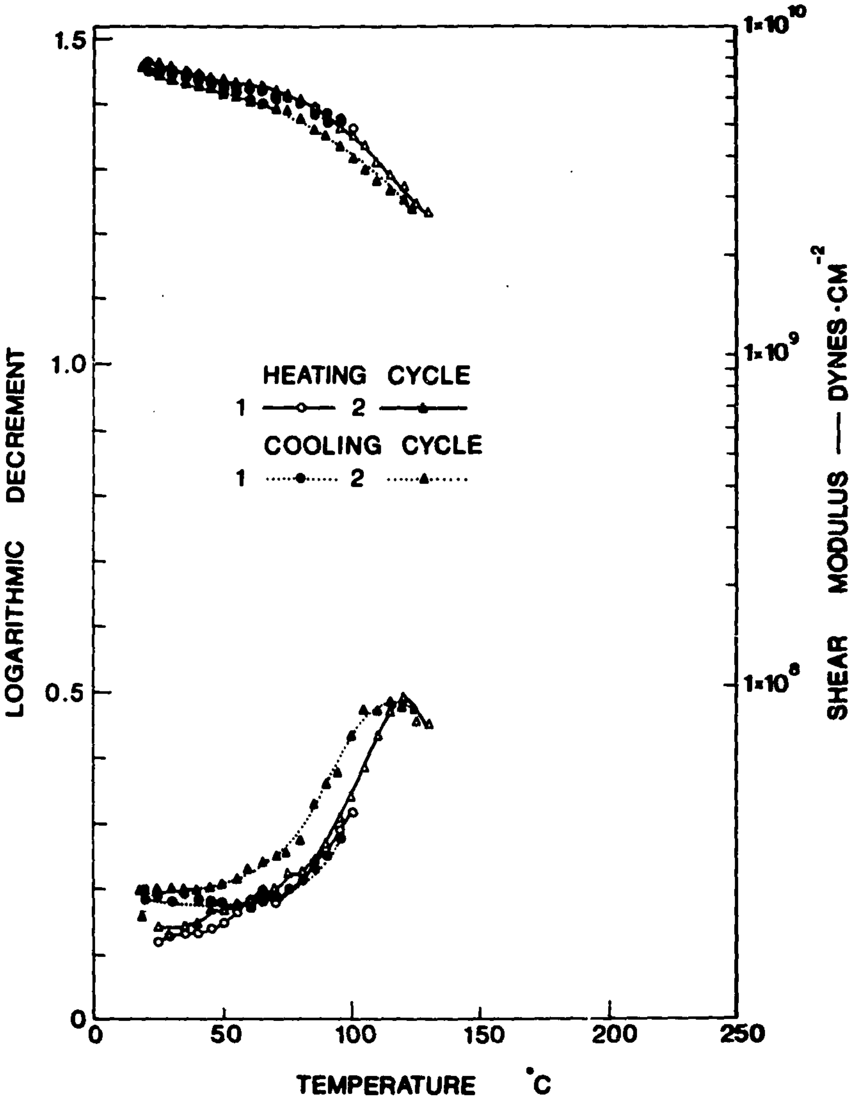

FIG. 33a

Effect of cyclic heating and cooling a spruce specimen in glycerol to 100°C and 130°C. The mechanical properties appear to be totally reversible up to 100°C.

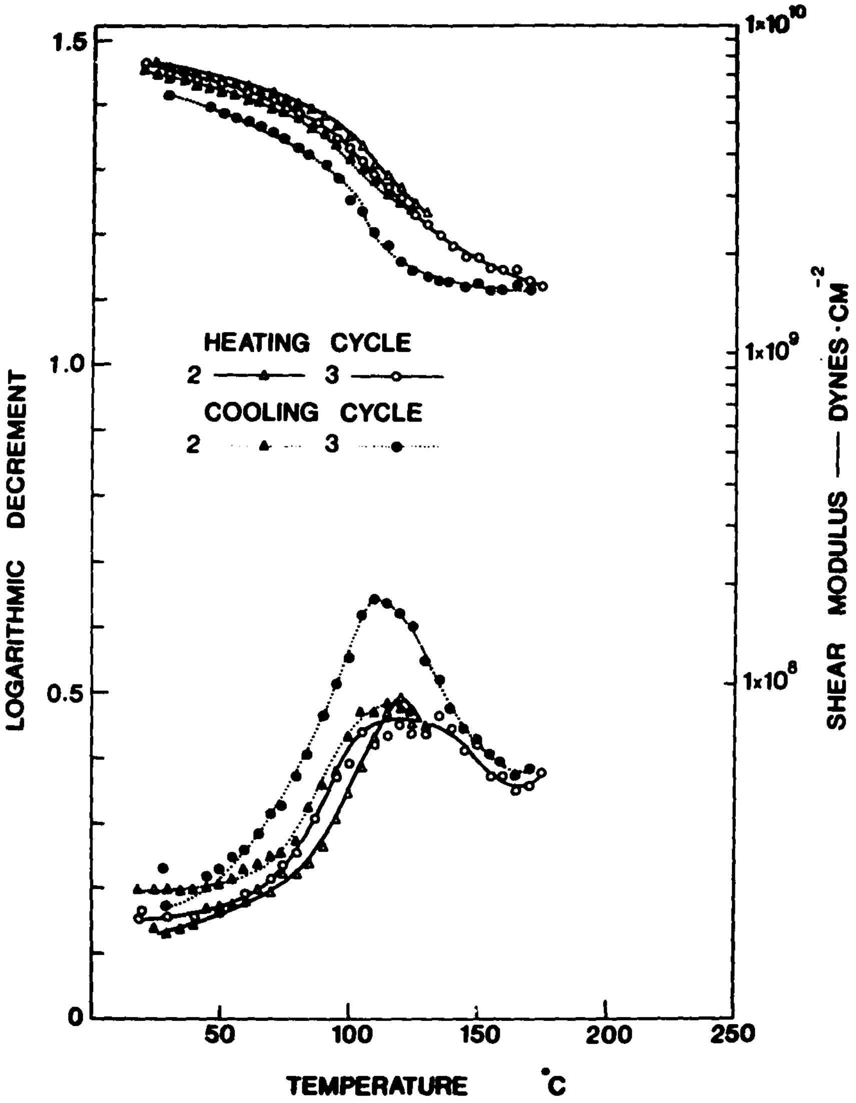

FIG. 33b

Effect of a further heating to 175°C and cooling. A small upward shift in the log decrement curve and downward shift in the shear modulus curve during the third heating cycle indicate some thermally induced irreversible change has occurred during the second cycle in the specimen. Data obtained during the cooling cycle are ignored owing to slight loosening of the sample in the clamps.

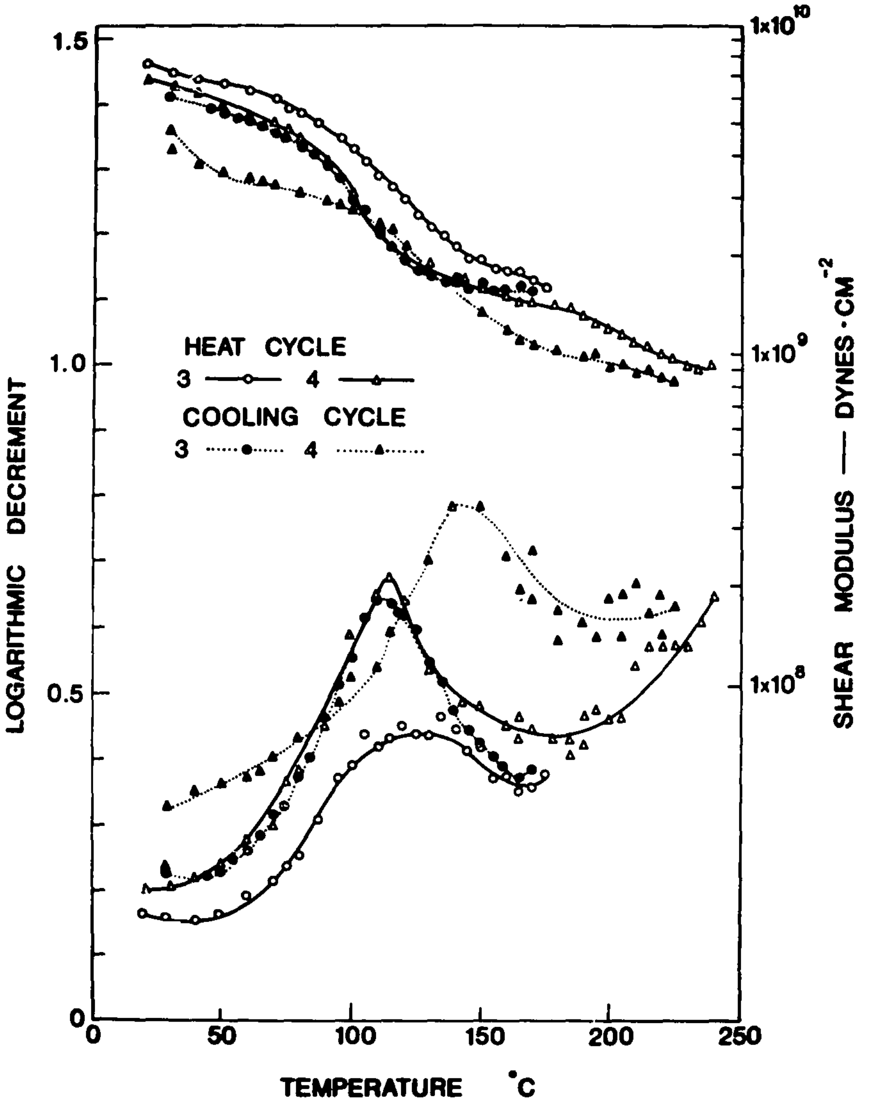

FIG. 33c

Effect of further heating to 240°C and cooling. Considerable shifts similar to those in Fig. 33b indicate a more pronounced irreversible change during the third heating cycle.

Results obtained during the second cooling cycle and all subsequent cooling cycles are suspect owing to loosening of the clamps and will not be considered further.

In the third heating cycle curves, shown in Fig. 32b, there is evidence of a slight irreversible change of structure leading to a higher decrement and a lower modulus. Curves obtained during the fourth heating cycle, shown in Fig. 33c, also show a large increase in decrement and a large decrease in modulus indicating that a large irreversible structural change has occurred when the specimen was maintained above the transition temperature for some time. It should be noted that data in the third and fourth cycles were obtained over periods of 10 and 14 hours respectively. Thus, in summary, the experiment shows that irreversible changes occur in spruce at or above the transition temperature and that the higher the temperature the more severe is the change.

One might suspect that irreversible changes occurring at high temperatures are time-dependent. To test this idea, measurements were made on an extracted black spruce specimen in glycerol, at two temperatures below 130°C and two above it, over various periods of time up to a maximum of four hours. The results are shown in Fig. 34. The log decrement and shear modulus values at 50°C and 100°C show little change with time. In fact, the slight change observed would indicate that the specimen is becoming somewhat stiffer. This is probably due

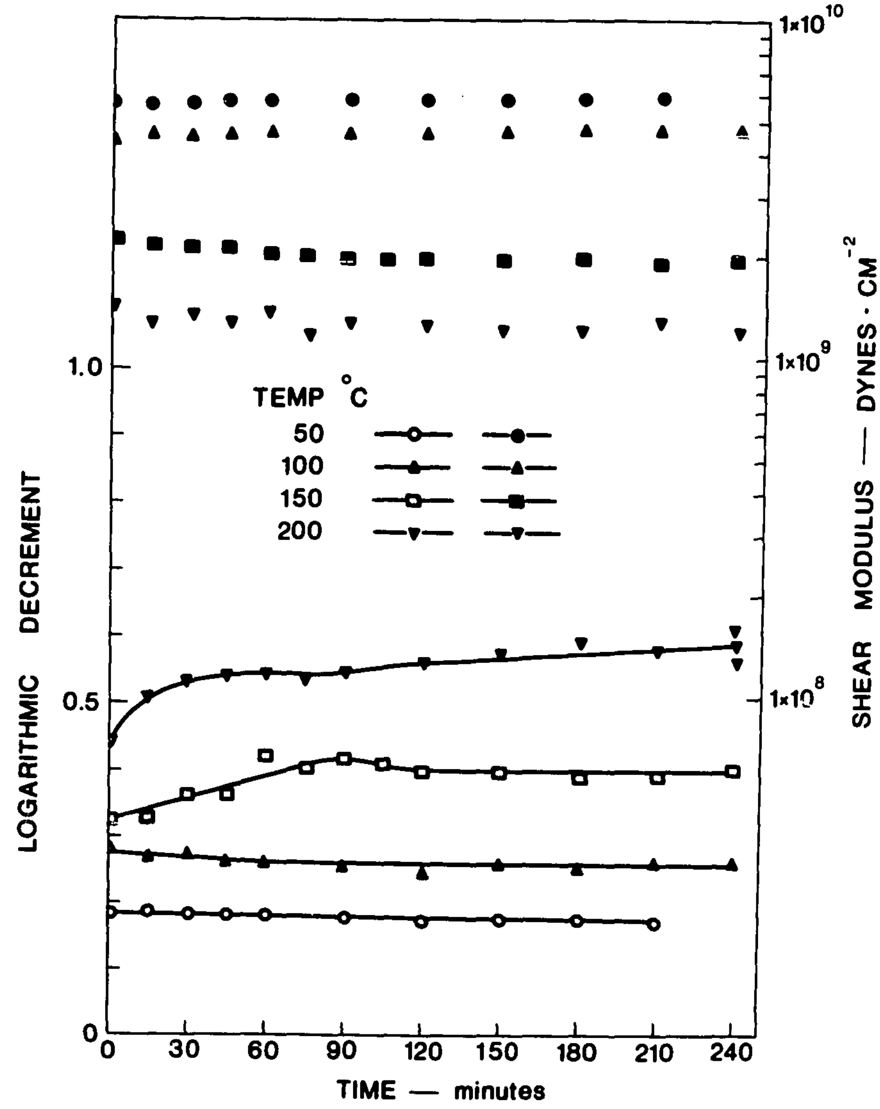

FIG. 34

Effect of heating time on the dynamic mechanical properties of an extracted spruce specimen in glycerol. The 50°C and 100°C curves show a small initial stiffening of the specimen with time. The 150°C and 200°C curves show a marked time dependent softening of the specimen for the first 60 minutes exposure, after which they level off somewhat.

to the replacement of water by glycerol in the specimen. At both 150°C and 200°C there is definitely a time dependent softening. This time dependence is most evident over the first hour after which it seems to level off for the 150°C curve. Similarly, for the curve at 200°C there is a marked time dependence during the first hour, followed by a slower softening over the next three hours.

DISCUSSION AND CONCLUSIONS

As is the case for air-dry samples of powdered spruce and birch, there is no evidence of a transition in whole dry samples of these species through the temperature range 20-220°C. Values of the shear modulus at room temperature are about 10^{10} dynes/cm^2, typical of most rigid polymers, and in good agreement with results of other measurements on the species reported in the literature (1,5). Since the shear strain is applied in the L-T and L-R planes, it will be appreciated that the modulus measured in these experiments is an average of the moduli in these two planes. However, the differences between these moduli are quite small (1) and for the purpose of this study it is not necessary to measure them individually, although a procedure for so doing is outlined in Appendix II. This appendix also includes a mathematical solution of the elastic torsional problem for a prismatic and in particular rectangular bar couched in such a manner that it is possible to introduce the anisotropy.

Values of the log decrement at room temperature are somewhat higher than those reported previously. This was thought to be due to a small frictional resistance to torsional oscillation originating in the two axial bearings supporting the shaft in the R.V.D.T. A comparison of results obtained for steel and aluminum with those reported in the literature (30) supported this idea, and it was possible to show that the frictional resistance was of the right order for a bearing of this type. Since this friction could not easily be eliminated, and since its contribution was reasonably constant it was decided not to make any correction for it. Bearing in mind all these considerations it can be concluded that the behaviour of whole dry wood through this temperature range is almost elastic. Although thermal softening of dry, isolated lignin and hemicelluloses has been shown to occur below 220°C there is no evidence of selective softening of these components in whole wood. This implies that the structural degradation of these components which is known to occur during their isolation is sufficient to reduce their glass transition temperatures from those they would exhibit in the native state. Conversely, it has been well established that increased crosslinking increases the glass transition temperature in other polymeric systems. Thus, since there is little doubt that lignin is more highly crosslinked in its native than its isolated state it is not surprising that no transition can be found in the whole wood. Even in powdered wood where the hemicellulose and lignin must have been mechanically degraded there is no thermal softening.

The cyclic heating and cooling experiments which were conducted on the whole samples show that small irreversible structural changes occur on heating. These are presumably related in some way to the thermal degradation processes which give rise to discoloration. In addition, there is some reversible thermally induced softening brought about by increased molecular motion of the amorphous matrix components with temperature.

Whole wood samples, like those of powdered wood, exhibit the onset of a transition in the region 220-240°C. In line with the thought expressed above, this transition is found to occur at a lower temperature and in a more clearly defined manner for the powdered samples. Thus, apart from effects which may arise from the extensive thermal degradation occurring through this temperature range, it is possible that this transition marks the co-operative softening of native lignin and hemicelluloses.

There is nothing particularly unusual in the overall effect, on the mechanical properties of spruce and birch, of swelling in water and glycerol. These liquids plasticize the wood structure and when the wood is strained movement of molecular segments of the amorphous polymer components which were frozen in the dry state can now take place quite freely. Segmental movements of this type dissipate strain energy as heat rather than storing it as potential energy. Thus, since the relief of stress in the strained state is a dissipative process it is time dependent. There are accompanying time dependent reductions of both elastic and loss moduli and a marked increase in mechanical damping.

Such behaviour is reflected in the temperature dependence of elastic shear moduli and log decrements of spruce and birch samples swollen in water and glycerol as seen in Figs. 15, 16, 20 and 21. It will be noted the shear modulus is lower and the log decrement higher for both water and glycerol swollen specimens than comparable dry specimens at room temperature. As the temperature is increased small transitions, attributed to the softening of hemicelluloses, are observed for both species in water below 90°C. A major transition is found for both species in glycerol at 130°C and this is attributed to lignin softening. These assignments are made entirely on the basis of Goring's findings on isolated components, although one might speculate in a similar vein on the basis that lignin is a much more crosslinked complex amorphous polymer than the hemicelluloses and hence one would expect it to soften at a higher temperature. In this context it is assumed that cellulose is completely crystalline and hence is not plasticized by either of the liquids.

Coincident with the rapid increase in log decrement on each of these curves there is a sigmoidal decrease in elastic shear modulus and the peak in decrement curve occurs at the same temperature as the inflexion point in the modulus curve. The difference between the curves obtained for water and glycerol has already been explained in terms of their relative effectiveness as plasticizers based in part upon their different molecular size. A further possible cause for these differences may be thought to arise from the viscous damping of the torsional oscillations in glycerol. This viscous resistance is similar to the frictional resistance of the R.V.D.T. bearings referred to previously, in that it only affects the values of log decrement and has no effect on the value of shear modulus. The viscous effect was found to be almost negligible even at room temperature.

As previously stated it was felt that steaming under pressure at a temperature in excess of 130°C might lead to some well defined structural change in the wood. The studies show that changes which occur as a result of such treatment are quite small, probably as a result of plastic flow of the hemicelluloses. Both species become somewhat less rigid, the spruce becomes slightly more elastic and the birch slightly less elastic. No permanent change in the lignin structure can be detected.

When lignin is selectively and progressively removed from the wood structure, at least two things occur simultaneously in both wood species. First, in the location where the lignin matrix is removed mechanical adhesion between the cellulose fibrils is weakened and the cell wall structure is opened up. Fergus (27) has shown that the initial stages of lignin removal occur preferentially in the middle secondary wall for both spruce and birch. Consequently, one would expect an accompanying decline in the contribution of this portion of the cell wall to the overall shear modulus. Further weakening of the cell wall in this manner will lead to further reduction in the modulus. Secondly, it is highly probable that the lignin remaining is degraded. As already stated, such degradation or reduction of crosslinking in the lignin which occurs prior to its dissolution will cause a reduction in its transition temperature. Although the relative contribution of these two processes cannot be determined from the results of these studies, there is little doubt that both occur.

Figs. 24-27 and 28-32 show the effects of progressive lignin removal on the temperature dependence of the mechanical properties of spruce and birch respectively. For both species the transition temperature decreases with increased lignin removal. When less than 1% of lignin is removed from spruce there is a drop of 30°C in the transition temperature as seen in Fig. 24. It is interesting to see such a large change is brought about by the removal of such a small amount of lignin and this would suggest that quite a dramatic change has occurred in the internal structure of the wood. This fact could have an important bearing on the production of ultra-high yield pulps from spruce. As more lignin is removed from spruce, the modulus decreases, the decrement increases and the transition temperature, originally at 130°C, moves as low as 40°C before finally disappearing. The onset of a higher transition is also apparent in all these curves. In untreated spruce this transition starts at about 180°C and is probably associated with the irreversible changes which were found to occur in the fracture studies (20,22). As lignin is removed the onset of this transition moves to lower temperatures. This behaviour is consistent with increased interfibril frictional resistance to the torsional oscillation. Naturally, such friction would also provide an increasing contribution to the mechanical damping at lower temperature as more lignin is removed. All these effects in spruce are progressive and continuous as a function of lignin removal.

In birch the same general effects occur, but not in the same continuous manner as in spruce. In fact, there are occasions when the sample appears to stiffen and become more elastic with additional lignin removal. This detailed behaviour warrants further investigation, and the only tentative explanation that can be offered at this time is that this apparent lack of continuous change in the mechanical properties results from a variability in the properties of the specimens chosen for the study.

Probably the most important single result of this study is that moist spruce and birch exhibit gross thermal softening at 130°C in glycerol. This softening temperature would be expected to be lower in steam, perhaps by about 10-15°C, and confirmatory measurements of this should be made in a pressurized steam atmosphere.

Furthermore, this temperature will vary with the rate of strain. Current measurements were conducted at a frequency of about 10 cps. In the mechanical refining process rates of strain with a frequency of about 10^6 cps. may be expected. According to the rule of thumb given in the introduction, thermal softening may be exploited at these high strain rates in steam at a temperature of about 140-150°C. One might expect that the nature of the pulps produced above and below this temperature would be significantly different, and this is what is actually found in the rapidly developing pressurized refining practice (17). The effect of different thermal and chemical pretreatments will provide valuable information towards the future development of this high yield pulping process.

CLAIMS TO ORIGINAL RESEARCH

1. Dynamic mechanical properties of dry and glycerol swollen spruce and birch were measured through the temperature range 20-240°C.

2. A major second-order transition was found at approximately 130°C for whole wood specimens of both species in the glycerol swollen state.

3. The effect of progressive delignification on temperature dependent mechanical properties of these wood species in glycerol was studied. It was found that the second-order transition temperature shifted to lower values with delignification.

4. A comparative study of water and glycerol as plasticizing agents for these wood species was made.

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APPENDIX I

The shape factor μ in the equation on page 32 is given by $\mu = \frac{16}{3}(1-0.63\frac{d}{b})$

Values of shape factor

Ratio of specimen width to thickness $\frac{b}{d}$	Shape factor μ
1.00	2.249
1.20	2.658
1.40	2.990
1.60	3.250
1.80	3.479
2.00	3.659
2.25	3.842
2.50	3.990
2.75	4.111
3.00	4.213
3.50	4.373
4.00	4.493
4.50	4.586
5.00	4.662
6.00	4.773
7.00	4.853
8.00	4.913
10.00	4.997
20.00	5.165
50.00	5.266
100.00	5.300
∞	5.333

APPENDIX II

When a rectangular wood specimen whose major axis is parallel to the grain is subjected to free torsional oscillations, stresses and strains are induced in the L-T and L-R planes of symmetry. Since the moduli in these planes are not the same for wood, the elastic shear modulus given by the equation on page 32 is in reality a composite-value of the two moduli. However, these moduli are nearly equal for these species and in effect they may be regarded, for the purpose of these studies, as two dimensional isotropic materials.

The equation for the shear modulus of a rectangular isotropic bar

$$G = \frac{38.54\ LI}{bd^3\ \mu\ p^2}\ \text{dynes/cm}^2 \qquad \text{(i)}$$

(see page 32)

is derived by substituting the expression for the restoring torque (31)

$$\text{Torque} = \frac{\mu}{16}\ G\theta bd^3 \qquad \text{(ii)}$$

into the equation of motion for free elastic torsional oscillations

$$IL\ddot{\theta} + \frac{\mu}{16}\ G\theta bd^3 = 0 \qquad \text{(iii)}$$

or $\ddot{\theta} + \omega^2\theta = 0$ where $\omega^2 = \frac{\mu G b d^3}{16}$

This is a well known periodic equation with a period

$$p = 2\pi/\omega \qquad \text{(iv)}$$

Substituting the expression for ω into (iv) gives (i).

A parallel solution to that given by Timoshenko and Goodier (31) for the problem of elastic, isotropic torsion for a prismatic and in particular rectangular bar is given below. This solution has been extended to include anisotropy. The problem is solved by the semi-inverse method. Certain assumptions regarding the deformation of the body are made and a solution is obtained which satisfies the equilibrium and boundary conditions. By appealing to uniqueness theorem of elasticity then this is the required solution.

Notation

X	are cartesian co-ordinates
u	are displacements
ε	are strains
σ	are stresses

(Suffixes refer to positive directions of axes 1, 2 and 3).

Assumptions

1. Since the bar is prismatic, the angle of twist for equal lengths parallel to the generators of the bar is the same for any twisting couple acting perpendicular to the bar. That is to say, every section of unit axial thickness rotates by the same amount.
2. Displacements of elements along a line parallel

to a generator are the same and proportional to the angle of twist. That is, displacement parallel to the axis of the bar is independent of its axial position.

We take X_3 co-ordinate as the axis of the bar, as shown in Fig. 1.

then $u_3 = \theta\psi(X_1X_2)$ (1)

where θ = angle of twist per unit length

and ψ is a function of X_1 and X_2 only

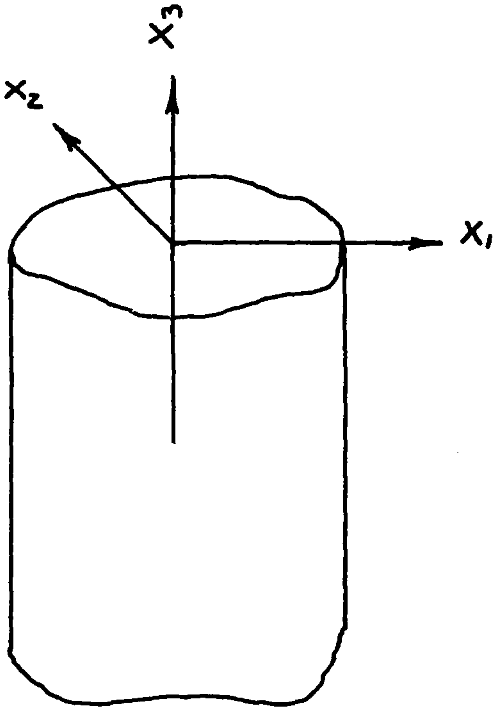

FIG. 1

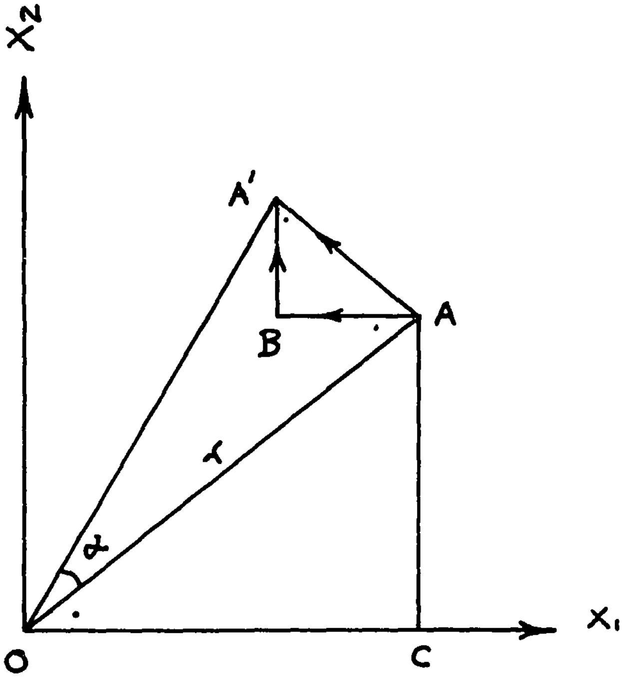

FIG. 2
Displacement of element A in X_1X_2 plane

Displacements

The displacement of an infinitesimal element A in the X_1X_2 plane at a distance X_3 along the bar and at a distance r from the X_3 axis is shown in Fig. 2. The section has twisted through an angle α, moving the point A to A'

then $\alpha = X_3\theta$

displacement $AA' = r\alpha = rX_3\theta$

The triangles AA'B and OAC are similar as the three lines of the triangles are mutually perpendicular,

therefore $$\frac{r}{rX_3\theta} = \frac{X_1}{BA'} = \frac{X_2}{AB}$$

or $$\frac{1}{X_3\theta} = \frac{X_1}{u_2} = \frac{X_2}{-u_1}$$

i.e. $$\left.\begin{aligned} u_1 &= -X_2X_3\theta \\ u_2 &= X_1X_3\theta \\ u_3 &= \theta\psi \qquad \text{from (1)} \end{aligned}\right\} \quad (2)$$

The strain tensor is defined by

$$\varepsilon_{ij} = \frac{1}{2}\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right]$$

substituting in (2) gives

$$\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33} = \varepsilon_{12} \equiv 0$$

For an isotropic material of shear modulus G, the stresses are given by

$$\sigma_{13} = \sigma_{31} = G\left[\frac{\partial u_1}{\partial X_3} + \frac{\partial u_3}{\partial X_1}\right]$$

$$= G\theta\left[-X_2 + \frac{\partial \psi}{\partial X_1}\right] \qquad (3a)$$

and

$$\sigma_{23} = \sigma_{32} = G\left[\frac{\partial u_2}{\partial X_3} + \frac{\partial u_3}{\partial X_2}\right]$$

$$= G\theta\left[X_1 + \frac{\partial \psi}{\partial X_2}\right] \qquad (3b)$$

These are the only stresses acting in the body since the strains are identically zero in other directions. Eliminating ψ from the above

we have

$$\frac{\partial \sigma_{23}}{\partial X_1} - \frac{\partial \sigma_{13}}{\partial X_2} = 2G\theta \qquad (3c)$$

<u>Equilibrium condition</u>

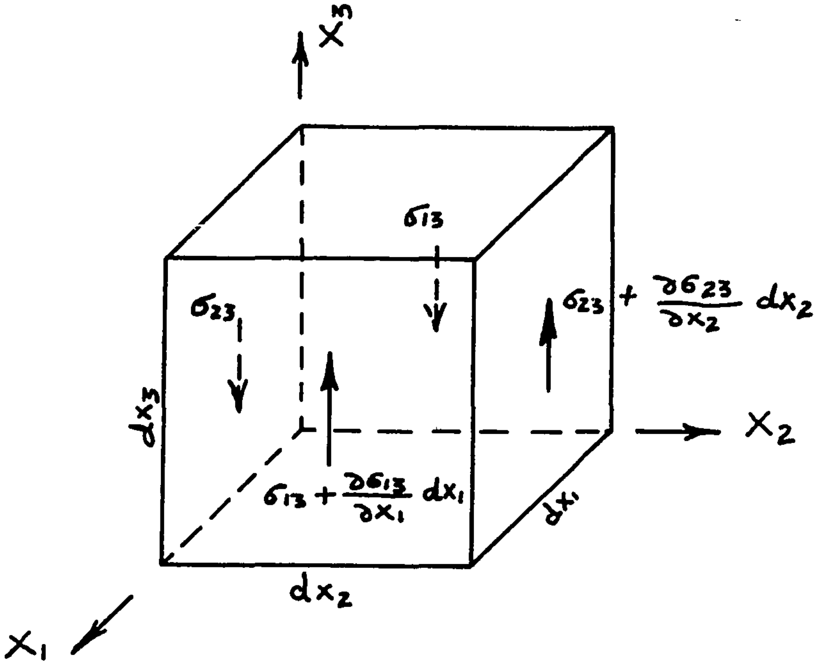

FIG. 3

Consider the vertical equilibrium of the stresses acting on a small cubical element $dX_1\ dX_2\ dX_3$ as shown in Fig. 3. Then for equilibrium of the element

$$(\sigma_{23} + \frac{\partial\sigma_{23}}{\partial X_2}\, dX_2 - \sigma_{23})dX_1 dX_3 + (\sigma_{13} + \frac{\partial\sigma_{13}}{\partial X_1}\, dX_1 - \sigma_{13})dX_2 dX_3 = 0$$

or

$$\frac{\partial\sigma_{13}}{\partial X_1} + \frac{\partial\sigma_{23}}{\partial X_2} = 0 \qquad (4)$$

Since there are no direct stresses and the shear stresses in the X_1X_2 planes are identically equal (strains and therefore stresses are independent of the X_3 co-ordinate), the equilibrium in the other directions is also satisfied.

Specify a stress function ϕ to satisfy the equilibrium condition (4) as follows:

$$\sigma_{13} = \frac{\partial\phi}{\partial X_2}$$

$$\text{and } \sigma_{23} = -\frac{\partial\phi}{\partial X_1} \qquad (5)$$

and substitute in (3c) to obtain

$$\frac{\partial^2\phi}{\partial X_1{}^2} + \frac{\partial^2\phi}{\partial X_2{}^2} = -2G\theta \qquad (6)$$

as the equation for the stress function.

Boundary conditions

The boundary is free from any normal restraining forces since there are no direct stresses acting in the body.

We apply the condition that the shear stresses along the boundary should not produce a force acting across the boundary of the bar, that is, it should be tangential to the boundary. Consider the forces acting on a small element near the boundary in the X_1X_2 plane of area dA as shown in Fig. 4.

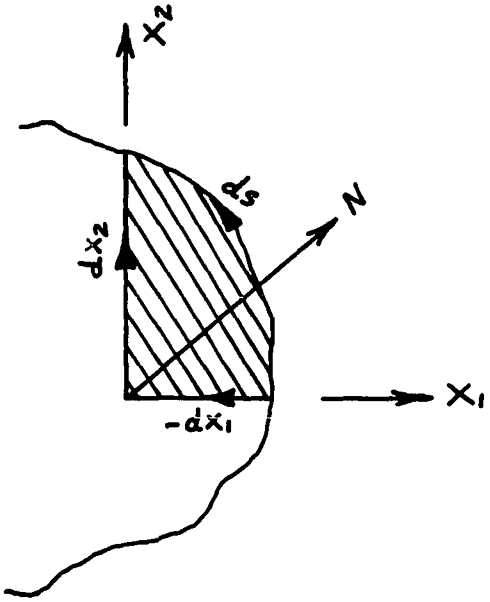

FIG. 4

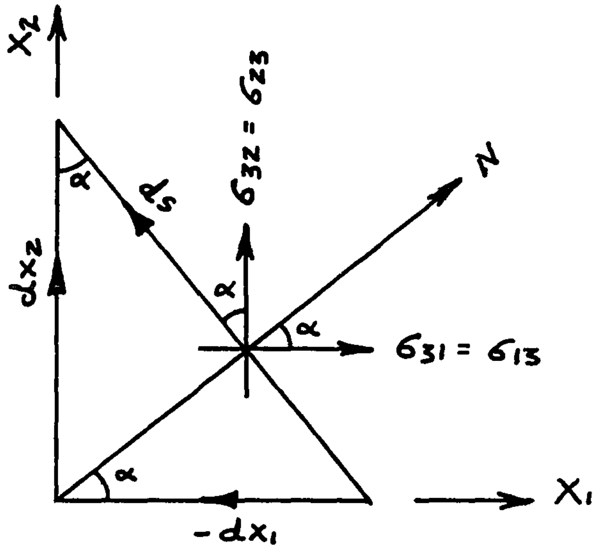

FIG. 4a

Area dA idealized and enlarged

Resolving shear forces normal to the boundary we must have

$$\sigma_{13}\ dA \cos\alpha + \sigma_{23}\ dA \sin\alpha = 0$$

From Fig. 4a

$$\cos\alpha = \frac{dX_2}{ds}$$

$$\sin\alpha = -\frac{dX_1}{ds}$$

and substituting for σ_{13} and σ_{23} from (5)

we have
$$\frac{\partial \phi}{\partial X_2}\frac{dX_2}{ds} + \left[-\frac{\partial \phi}{\partial X_1}\right]\left[-\frac{dX_1}{ds}\right] = 0$$

$$\text{or} \quad \frac{d\phi}{ds} = 0 \qquad (7)$$

Thus, to meet the boundary condition ϕ must be constant along the boundary. We take ϕ to be zero on the boundary without any loss of generality.

To show that the stress function ϕ gives a pure couple, consider the result of the shear stresses along X_1 direction.

$$\text{the resultant} = \iint_{\text{area}} \sigma_{31}\, dX_1 dX_2$$

$$= \iint \frac{\partial \phi}{\partial X_2}\, dX_1 dX_2$$

$$= \int dX_1 \int \frac{\partial \phi}{\partial X_2}\, dX_2$$

$$= \int dX_1 \int d(\phi)$$

$$= \int (\phi_m - \phi_\ell)\, dX_1$$

where m and ℓ are the limits of integration on the boundary,

but $\phi_m = \phi_\ell$ as ϕ is constant on the boundary.

Hence, resultant along the X_1 direction = 0.

Similarly for the X_2 direction.

The moment produced by the shear stresses in the bar is opposed by the torque T acting on the bar, thus:

$$T = \iint_{area} (\sigma_{32}X_1 - \sigma_{31}X_2)dX_1dX_2$$

$$= \iint - \frac{\partial \phi}{\partial X_1} X_1 \; dX_1dX_2 - \iint \frac{\partial \phi}{\partial X_2} X_2 \; dX_1dX_2$$

$$= - \int dX_2 \int X_1 \; d(\phi) - \int dX_1 \int X_2 \; d(\phi)$$

Integrating by parts

$$T = -[\int dX_2\{X_1(\phi)_m^i - \int \phi \; dX_1\}]$$

$$-[\int dX_1\{X_2(\phi)_k^j - \int \phi \; dX_2\}]$$

but since $(\phi)_m^i = (\phi)_k^j = 0$ as before

$$T = 2 \iint_{area} \phi \; dX_1dX_2 \qquad (8)$$

Thus, it is shown that the stress function ϕ satisfies the equilibrium and boundary conditions and produces a pure couple. By appealing to the uniqueness theorem, the solution for a prismatic bar in elastic torsion is as given above.

The forces applied to the end of the bar must be distributed in such a manner that they oppose the shear stress field, i.e. the stresses σ_{31} and σ_{32}. However, the stress function should give true values of stresses and strains at a sufficient distance from the end when this condition is not satisfied by appealing to Saint-Venant's principle.

Solution for a bar of rectangular cross-section

Seek a solution for a rectangular boundary of width b and thickness t by using the Prandtl stress function,

that is,

$$\nabla^2 \phi = -2G\theta \qquad (6)$$

Since ϕ is zero on a boundary symmetrical with respect to X_1 and X_2 axes a function of similar properties should be suitable. We expand the right hand side of (6) as a Fourier double sine series.

Thus,

$$\nabla^2 \phi = -2G\theta(1\text{x}1)$$

$$= -2G\theta \frac{16}{\pi^2} \sum_{\substack{m \\ \text{odd}}}^{\infty} \sum_{n}^{\infty} \frac{1}{mn} \sin\frac{m\pi X_1}{b} \sin\frac{n\pi X_2}{t}$$

and the solution for ϕ is

$$\phi = \frac{32G\theta}{\pi^2} \sum_{\text{odd}}\sum \frac{\sin\frac{m\pi X_1}{b} \quad \sin\frac{n\pi X_2}{t}}{mn\left[\frac{m^2\pi^2}{b^2} + \frac{n^2\pi^2}{t^2}\right]} \qquad (9)$$

as can be seen by direct differentiation of (9)

$$\text{or} \quad \frac{32G\theta}{\pi^4} \sum_{\text{odd}}\sum \frac{1}{mn} \frac{\sin\frac{m\pi X_1}{b} \quad \sin\frac{n\pi X_2}{t}}{\frac{m^2}{b^2} + \frac{n^2}{t^2}}$$

$$\text{and} \quad T = \frac{64G\theta}{\pi^4} \iint \sum_{\text{odd}}\sum \frac{1}{mn} \frac{\sin\frac{m\pi X_1}{b} \quad \sin\frac{n\pi X_2}{t}}{\frac{m^2}{b^2} + \frac{n^2}{t^2}}$$

$$= \frac{64G\theta}{\pi^4} \sum\sum_{odd} \frac{\cos\frac{m\pi X_1}{b}\Big|_b^o \cos\frac{n\pi X_2}{t}\Big|_t^o}{mn\left[\frac{m^2}{b^2} + \frac{n^2}{t^2}\right]\frac{m\pi}{b}\,\frac{n\pi}{t}}$$

$$= \frac{256G\theta bt^3}{\pi^6} \sum\sum_{odd} \frac{1}{m^2n^2\left[\frac{m^2}{K^2} + n^2\right]} \qquad (10)$$

where $K = \frac{b}{t}$.

The series converges rapidly. This equation is equivalent to (ii).

Anisotropy of wood

When we consider wood as a material with three planes of symmetry, the number of independent elastic constants increases from the two in isotropic case to nine. This can be shown by considering the invariance of the strain energy function in the planes of symmetry.

The strain energy function is: (32)

$$\begin{aligned}
2W = {} & C_{11}\varepsilon^2X_1X_1 + 2C_{12}\varepsilon X_1X_1\varepsilon X_2X_2 + 2C_{13}\varepsilon X_1X_1\varepsilon X_3X_3 + 2C_{14}\varepsilon X_1X_1\varepsilon X_2X_3 \\
& + 2C_{15}\varepsilon X_1X_1\varepsilon X_3X_1 + 2C_{16}\varepsilon X_1X_1\varepsilon X_1X_2 \\
& + C_{22}\varepsilon^2X_2X_2 + 2C_{23}\varepsilon X_2X_2\varepsilon X_3X_3 + 2C_{24}\varepsilon X_2X_2\varepsilon X_2X_3 \\
& + 2C_{25}\varepsilon X_2X_2\varepsilon X_3X_1 + 2C_{26}\varepsilon X_2X_2\varepsilon X_1X_2 \\
& + C_{33}\varepsilon^2X_3X_3 + 2C_{34}\varepsilon X_3X_3\varepsilon X_2X_3 + 2C_{35}\varepsilon X_3X_3\varepsilon X_3X_1 + 2C_{36}\varepsilon X_3X_3\varepsilon X_1X_2 \\
& + C_{44}\varepsilon^2X_2X_3 + 2C_{45}\varepsilon X_2X_3\varepsilon X_3X_1 + 2C_{46}\varepsilon X_2X_3\varepsilon X_1X_2 \\
& + C_{55}\varepsilon^2X_3X_1 + 2C_{56}\varepsilon X_3X_1\varepsilon X_1X_2 + C_{66}\varepsilon^2X_1X_2 \qquad (11)
\end{aligned}$$

consider reflection in X_1X_2 plane,

$$X_1' = X_1,\ X_2' = X_2 \text{ and } X_3' = -X_3$$

Where the primes denote the reflected axes

or $\varepsilon X_1'X_1' = \varepsilon X_1X_1$, $\varepsilon X_2'X_2' = \varepsilon X_2X_2$, $\varepsilon X_3'X_3' = \varepsilon X_3X_3$

$\varepsilon X_1'X_2' = \varepsilon X_1X_2$, $\varepsilon X_2'X_3' = -\varepsilon X_2X_3$, $\varepsilon X_3'X_1' = -\varepsilon X_3X_1$

substituting in (11) and applying condition of invariance

$$C_{14} = C_{15} = C_{24} = C_{25} = C_{34} = C_{35} = C_{45} = 0$$

similarly for X_2X_3 plane

$\varepsilon X_1'X_2' = -\varepsilon X_1X_2$ and $\varepsilon X_3'X_1' = -\varepsilon X_3X_1$, others equal

and give

$$C_{15} = C_{16} = C_{25} = C_{26} = C_{35} = C_{36} = C_{45} = C_{46} = C_{56} = 0$$

and for X_3X_1 plane

$\varepsilon X_1'X_2' = -\varepsilon X_1X_2$ and $\varepsilon X_2'X_3' = -\varepsilon X_2X_3$ others being equal

and give

$$C_{14} = C_{16} = C_{24} = C_{26} = C_{34} = C_{36} = C_{46} = C_{56} = 0$$

leaving

C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55} and C_{66}

as the independent constants. These are the three Young's moduli, the three Poisson's ratios and the three shear moduli in the three planes of symmetry.

We denote the shear moduli in

X_1X_3 plane by G_1

and X_2X_3 plane by G_2 for an anisotropic bar.

Since the displacements and strains are not affected by anisotropy, the only strains in the bar undergoing torsion are

$$\varepsilon_{23} = \theta\left[\frac{\partial\psi}{\partial X_2} + X_1\right]$$

and $$\varepsilon_{13} = \theta\left[\frac{\partial\psi}{\partial X_1} - X_2\right]$$ as before

the stresses are

$$\begin{aligned}\sigma_{23} &= G_2\theta\left[\frac{\partial\psi}{X_2} + X_1\right]\\ \sigma_{13} &= G_1\theta\left[\frac{\partial\psi}{\partial X_1} - X_2\right]\end{aligned} \qquad (12)$$

We eliminate ψ by differentiating σ_{23} with respect to X_1 and multiplying by G_1 and differentiating σ_{13} with respect to X_2 and multiplying by G_2 and subtracting.

Thus,

$$\frac{G_1\partial\sigma_{23}}{\partial x_1} - \frac{G_2\partial\sigma_{13}}{\partial x_2} = 2G_1G_2\theta \qquad (13)$$

The equilibrium condition is not affected by the anisotropy and by defining ϕ as before, we have:

$$G_1\,\frac{\partial^2\phi}{\partial x_1{}^2} + G_2\,\frac{\partial^2\phi}{\partial x_2{}^2} = -\,2G_1G_2\theta \qquad (14)$$

The boundary conditions will still be satisfied if ϕ is constant along the boundary.

We again expand the right hand side of (14) in double sine series.

The solution for ϕ is

$$\phi = \frac{32G_1G_2\theta}{\pi^2}\sum_{\substack{m\\ \text{odd}}}^{\infty}\sum_{n}^{\infty}\frac{1}{mn}\,\frac{\sin\frac{m\pi X_1}{b}\,\sin\frac{n\pi X_2}{t}}{G_1\frac{m^2\pi^2}{b^2}+G_2\frac{m^2\pi^2}{t^2}} \qquad (15)$$

The equation for torque remains

$$T = 2\iint \phi\, dX_1 dX_2$$

$$\therefore\ T = \frac{256G_1G_2\theta}{\pi^6}\sum\sum\frac{1}{\frac{m^2n^2}{bt}\left[\frac{G_1m^2}{b^2}+\frac{G_2n^2}{t^2}\right]}$$

$$= \frac{256G_1\theta bt^3}{\pi^6}\sum\sum\frac{1}{m^2n^2\left[\frac{m^2}{K^2}+n^2\right]}$$

Where K is now defined as $\sqrt{\frac{G_2}{G_1}}\,\frac{b}{t}$

and G_1 is the shear modulus in the width length plane of the bar.

The above expression for torque can be related to the period of free torsional oscillation as before. The two shear moduli can be evaluated by conducting tests on two specimens with different width to thickness ratios. G_1 and G_2 can then be found by method of successive approximations (1). A value of G_1/G_2 is first assumed from which approximate values for the moduli can be calculated which in turn will give a better approximation, and so on.