

Some Physical Properties of Films Made from Cellulose Dissolved in Solutions of Nitrogen Dioxide in Dimethylformamide

A. VENKATESWARAN and L. P. CLERMONT, *Department of The Environment, Canadian Forestry Service, Eastern Forest Products Laboratory, Ottawa, Canada*

Synopsis

Water-soluble films of cellulose nitrate-nitrite were prepared by dissolving bleached sulfite pulp in a solution of nitrogen dioxide in dimethylformamide (DMF) at room temperature and heating the solution at 70°C for about 3 hr. Their water sorption, fine structure, and electrical properties were measured and compared with those of three other films—one water soluble (poly(vinyl alcohol)) and two water insoluble (cellophane and a film prepared from a cellulose solution in the nitrogen dioxide-DMF mixture and cast immediately after the cellulose had dissolved at room temperature). A comparison between the properties of water-soluble films and the poly(vinyl alcohol) film showed that the former had higher crystallinity, lower moisture absorption in the 0-80% relative humidity region, lower permittivity and a.c. conductance, and higher d.c. resistance. The DMF-cast water-insoluble film adsorbed less moisture than the cellophane film.

INTRODUCTION

Cellulose derivatives, soluble or insoluble in water, can be prepared by dissolving bleached sulfite pulp in a solution of nitrogen dioxide in dimethylformamide (DMF). A previous communication¹ reported that cellulose derivatives soluble in water and in dilute alkali may be prepared by dissolving bleached sulfite pulp in the above solution at room temperature and heating this viscous solution at 70°C for 2 to 3 hr. These water-soluble cellulose derivatives were mixed nitrate-nitrite esters with degrees of substitution ranging from 0.47 to 0.55. Degrees of polymerization were in the range 200 to 300. No evidence of appreciable cellulose oxidation was found. These films can be prepared quickly to any desired thickness in the laboratory.

Cellulose dissolved in a nitrogen dioxide solution in DMF may be recovered by precipitation into methanol or water practically unreacted, after a short treatment time at room temperature.^{2,3} Water-insoluble films may be prepared from these cellulose solutions.

Since there is a trend in the electrical industry to replace certain insulating papers, such as capacitor paper, with films, it is of considerable interest to evaluate the moisture sorption, electrical properties, and crystalline nature of these new cellulose films both soluble and insoluble in water.

EXPERIMENTAL

A commercial bleached sulfite pulp was used having a D.P. of about 700 and an α -cellulose content of 85.0%. The pulp, in sheet form, was disintegrated in a Waring Blendor, washed with acetone, air dried, and fluffed by running it through a small hammer mill.

The DMF was dried over anhydrous sodium sulfate and distilled under vacuum at 60°C.

Nitrogen dioxide gas was used without further purification from a cylinder.

Bleached sulfite pulp was dissolved, at room temperature, in a solution of nitrogen dioxide in DMF and treated at 70°C as reported previously.¹ The clear solution was cooled to room temperature, and a film was cast by pouring the solution onto a glass plate. A glass rod with a copper wire wound around each end was used as a draw bar. Regeneration was done in methanol followed by rinsing with fresh methanol until neutral.

The DMF-cast film was air dried at room temperature.

Cellulose was regenerated from the same clear DMF solution by pouring it into 2 to 3 volumes of methanol. The resulting precipitate was washed with methanol until free of acid and dried in a vacuum oven at 50°C. The dried powder was then dissolved in distilled water, and films were prepared by casting onto a chrome-plated steel plate and drying in air at room temperature overnight. Both types of films were prepared from 2% (w/v) solutions of cellulose ester. The films varied in thickness from 13 to 20 μ .

Water-insoluble films were prepared by casting the clear DMF solution onto a glass plate immediately after the cellulose had completely dissolved (about 20 min) at room temperature and regenerating in a water bath.

The water sorption of all films was determined between 0% and 100% relative humidities (R.H.). Duplicate samples of the films were first vacuum dried ($<10^{-4}$ torr) and conditioned to various R.H. values either over atmospheres of suitable, saturated salt solutions^{4,5} or in a controlled humidity room.

X-Ray diffractograms of all films were recorded using a Norelco x-ray diffraction spectrometer with parafocusing geometry. The collimated beam was defined by a divergence slit of 1° angular aperture at the x-ray port. The diffracted beam was defined by a 0.024-in. receiving slit and a 1° angular aperture scatter slit. The diffracted signal was received by a Geiger counter tube and recorded with a Brown recording potentiometer. Rectangular samples⁶ (4 cm \times 3 cm \times 0.0254 cm) were placed in a holder and then mounted on the goniometer. The diffraction intensity was measured from $2\theta = 8^\circ$ – 26° to include the three main diffraction maxima of the cellulose lattice structure: the (101), (10 $\bar{1}$), and (002) planes. To eliminate the error due to possible misalignment of the samples in the holder, tests were repeated after rotating the samples through 90°.

Permittivity and conductivity of the films at 10^4 and 10^5 Hz and d.c. resistance were determined over a moisture content range of 0% to 16%. For a.c. measurements, a GR 1615A capacitance-conductance bridge with

conventional accessories was used. The electrical parameters were measured with a highly accurate ($>99.5\%$) three-electrode system.^{7,8} For measurements in a d.c. field, a 610C Keithley electrometer was used. The electrode diameter was 5 cm, and the electrode gap varied between 0.152 and 0.203 mm.

RESULTS AND DISCUSSION

Water Sorption-Desorption Studies

A comparison of Figures 1 and 2 shows that with water-soluble films, the DMF-cast film absorbs more moisture than the water-cast film. This is because the DMF-cast film was prepared directly from a DMF solution which has a considerably higher swelling ability than water from which the latter film was prepared. This means that the DMF-cast film has a more

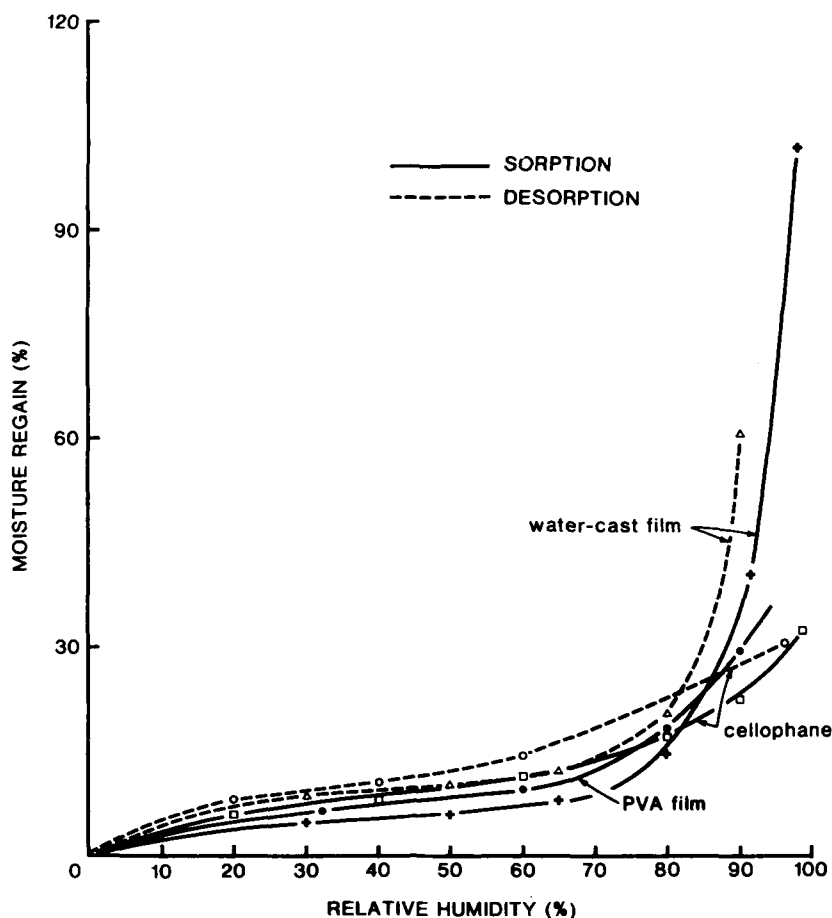


Fig. 1. Sorption-desorption curves for water-cast cellulose nitrate-nitrite, poly(vinyl alcohol), and cellophane films.

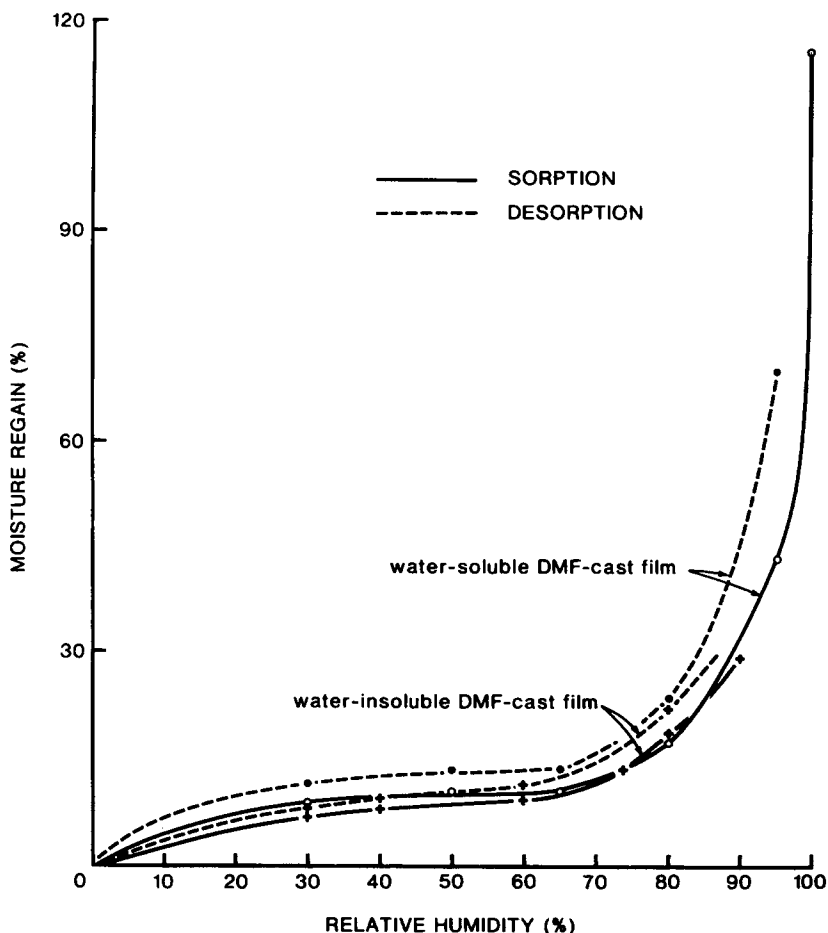


Fig. 2. Sorption-desorption curves for water-soluble and water-insoluble DMF-cast cellulose nitrate-nitrite films.

open structure, is more accessible to reagents, and has a lower degree of crystallinity than the water-cast film. The fact that the latter was air dried from a water solution may explain, in part, its higher crystallinity. Contact with water and subsequent drying in air is known to induce partial recrystallization in a cellulosic material.⁹ Figure 2 also shows that the water-insoluble film absorbs the least moisture, which means that it has a higher crystallinity than water-soluble films.

X-Ray Diffraction

X-Ray diffractograms of the three films are shown in Figure 3. Since these films were prepared from regenerated cellulose, the diffractograms are expected to be similar to that of cellulose II. In cellulose I, the diffraction intensity of the (002) plane occurs as a sharp peak at 22.4° (2θ). In regenerated cellulose, since the molecules are displaced relative to one another

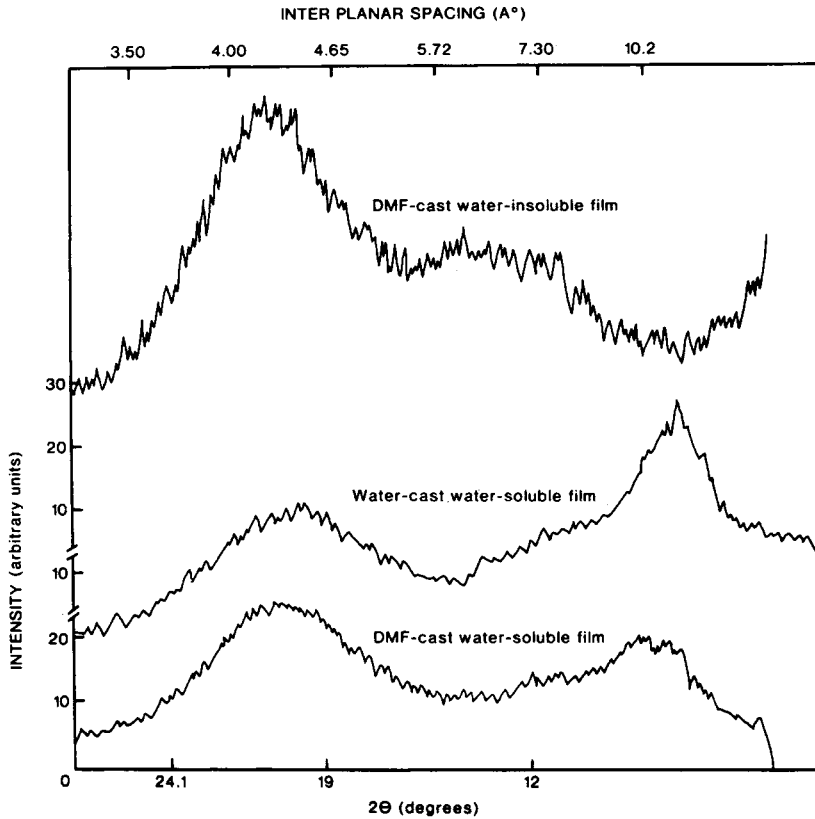


Fig. 3. X-Ray diffractograms of the new films.

along the a -axis and rotated about 30° out of the ab plane, there is a lattice shift, and the diffraction intensity of the (002) plane occurs at about 21° .¹⁰ A minor shift due to solvent treatment also occurs.

A higher diffraction intensity in the (002) plane usually indicates a higher crystalline structure of the material.^{10,11} According to this view, the three films (Fig. 3) may be arranged in the following order with regard to their crystalline nature:

water-insoluble film > water-cast film > DMF-cast film

Variation of Permittivity, Conductivity, and d.c. Resistance of the Films With Moisture Content

Electrical measurements on all films were made on vacuum-dried samples at moisture contents of up to 16%, by exposing the films to various R.H. values. Variation of permittivity and conductivity of the films with moisture are given in Figures 4 and 5. The variation of d.c. resistance with moisture is shown in Figure 6.

TABLE I
Dielectric Properties of Dry Films

Sample	Density, g/cc	Permittivity ϵ_0		a.c. Conductivity, mho/cm ¹		Permittivity ϵ_1 ¹		d.c. Resistance, ohms
		10 ⁴ Hz	10 ⁵ Hz	10 ⁴ Hz	10 ⁵ Hz	(corrected to 1 g/cc) 10 ⁴ Hz	10 ⁵ Hz	
Water-insoluble	0.755	2.45	2.35	5.6×10^{-11}	8.9×10^{-10}	2.92	2.79	1.6×10^{12}
DMF-cast ^a	0.860	4.00	3.80	6.0×10^{-10}	8.0×10^{-9}	4.49	4.26	5.0×10^{10}
Water-cast	0.900	3.6	3.30	4.0×10^{-10}	5.0×10^{-9}	3.89	3.56	7.0×10^{11}
Cellophane	1.490	6.4	6.0	1.1×10^{-9}	5.6×10^{-8}	4.62	4.36	—
PVA	1.296	10.0	8.2	5.6×10^{-9}	6.1×10^{-8}	7.94	6.54	1.0×10^{10}

^a Water-soluble film.

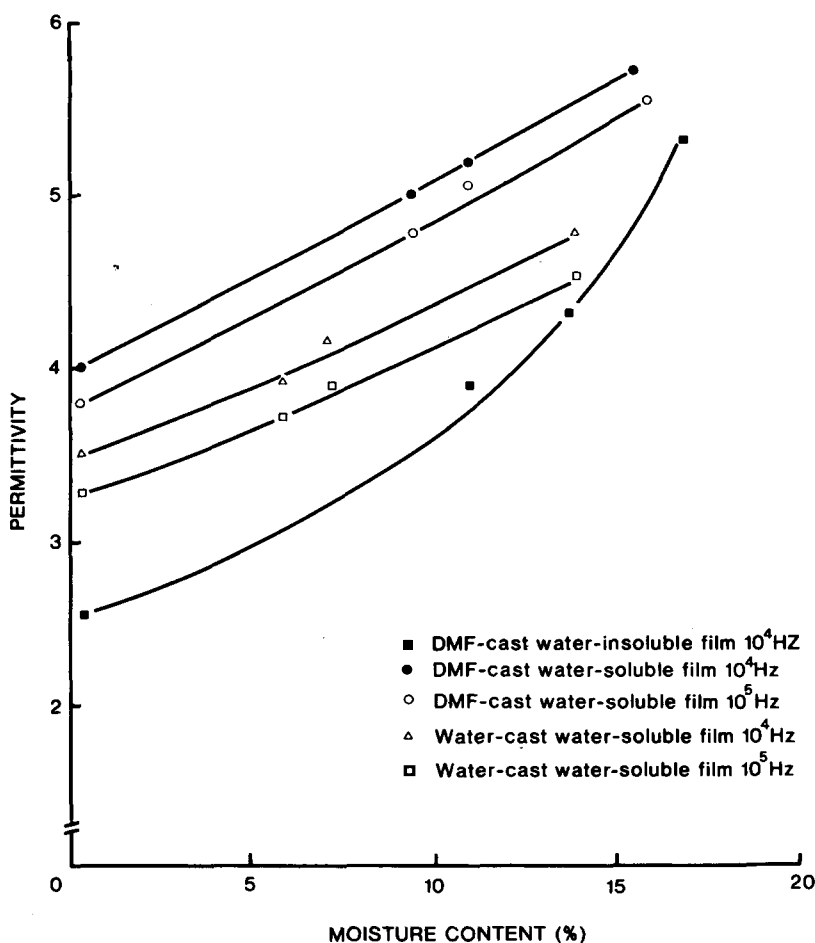


Fig. 4. Variation in permittivity with moisture content of water-soluble DMF- and water-cast films, and a water-insoluble film at several frequencies.

Among the various films prepared from a cellulose solution in NO_2 -DMF and tested for electrical properties (Figs. 4, 5, and 6; Table I), the water-insoluble film possesses the lowest permittivity and conductivity, and the highest resistivity, while the DMF-cast water-soluble film has the highest permittivity and conductivity, and the lowest resistivity. These results are interpreted to mean that the water-insoluble film contains fewer polar groups and molecular segments capable of vibration than the DMF-cast water-soluble film.

Comparison Between Moisture Sorption, Fine Structure, and Electrical Properties of the Various Films

Since the new films may be prepared in a water-soluble or a water-insoluble form, we compared the physical and electrical properties of these films with those of another water-soluble film, i.e., poly(vinyl alcohol)

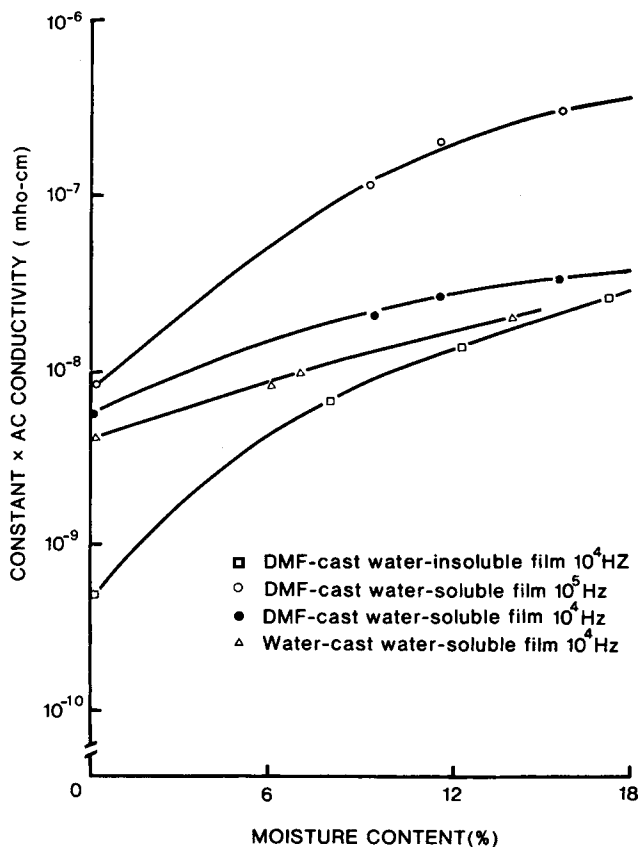


Fig. 5. Variation of a.c. conductivity with moisture content of water-soluble DMF- and water-cast films, and a water-insoluble film.

(PVA)^{11,12} and with those of cellophane.¹³ The sorption of PVA and the sorption-desorption of cellophane films are shown in Figure 1.

A comparison of the sorption of the new films (Figs. 1 and 2) with that of PVA and cellophane films disclosed the following:

1. The DMF-cast films and the PVA film behave quite similarly with regard to moisture sorption.
2. The water-cast film absorbs less moisture than the PVA film (up to 90% R.H.), which means that the former is more crystalline.
3. The cellulose nitrate-nitrite and PVA films have a greater ability to absorb moisture due to their water-soluble nature than the water-insoluble or cellophane film at all R.H. levels.

Table I gives the dielectric properties of all films studied. Permittivities of the films were corrected to an arbitrary unit density for comparison, using the following equation⁷:

$$\epsilon_1^1 = (\epsilon_0 - 1) \frac{d_1}{d_0} + 1$$

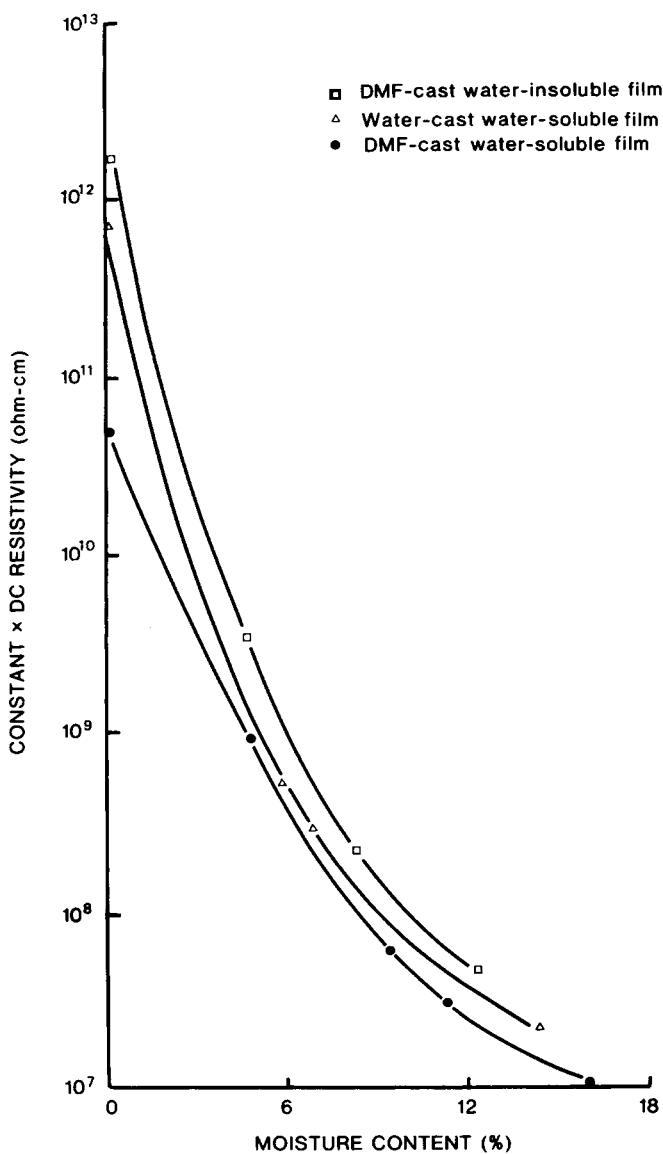


Fig. 6. Variation of d.c. resistivity with moisture content of water-soluble DMF- and water-cast films, and a water-insoluble film.

where ϵ_1 is the permittivity at unit density and ϵ_0 is the permittivity at the natural density d_0 . Since the effect of density on conductivity is small, this correction is neglected.¹⁴ A comparison of the electrical properties of the films shows that the water-insoluble film has lower permittivity, lower conductivity, and higher DC resistance than water-soluble films.

CONCLUSIONS

Mixed nitrate-nitrite ester films cast from water solutions were found to have higher crystallinity than those cast from DMF. Their moisture regain and x-ray measurements showed that they also had higher crystallinity than water-insoluble films. Water-insoluble films possess lower permittivity, lower conductivity, and higher resistance than cellophane. A fuller assessment of the merits of the new films in electrical applications, measurements on the aging characteristics of the film (particularly in oil over a conventional temperature range), and the dielectric breakdown of the impregnated film should be made.

References

1. L. P. Clermont and F. Bender, *J. Polym. Sci.*, **1-A**, 1969 (1972).
2. R. G. Schweiger, *Chem. Ind. (London)*, **10**, 296 (1969).
3. L. P. Clermont, *Can. Dept. Fish. Forest. Bi-Monthly Res. Notes*, **26**, 58 (1970).
4. R. T. Lin, Ph.D. Dissertation. State University College of Forestry, Syracuse University, N.Y., 1965.
5. F. F. Wangaard and L. A. Grandos, *Wood Sci. Technol.*, **1**, 253 (1967).
6. A. Venkateswaran, *J. Appl. Polym. Sci.*, **9**, 1167 (1965).
7. A. Venkateswaran, *J. Appl. Polym. Sci.*, **9**, 1127 (1965).
8. A. Venkateswaran, to be published.
9. M. Kouris, H. Ruck, and S. G. Mason, *Can. J. Chem.*, **36**, 931 (1958).
10. L. Segal and C. M. Conrad, *Amer. Dyestuff Rep.*, Aug. 26, (1957).
11. H. Tadokoro, S. Seki, and I. Nitta, *Bull. Chem. Soc. Japan*, **23**, 559 (1955).
12. K. Kawasaki, *J. Colloid Sci.*, **16**, 405 (1961).
13. L. T. Muus, *Trans. Danish A.T.S.*, No. 4 (1953).
14. A. Venkateswaran, *Wood Sci.*, **4**, 248 (1972).

Received November 28, 1972

Revised June 19, 1973