

## Thin Water Vapor Barriers for Paper

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### Synopsis

Low-pressure plasma technique was used in the deposition of thin polymeric coatings upon a filter paper. Sixteen different monomers, including aromatic and aliphatic hydrocarbons, nitriles, chlorine-containing compounds, and a silane, were used in the coatings. Most of the coatings functioned as water vapor barriers in different degrees, and the coated samples possessed wet tensile strengths anywhere from 3 to 34 times that of the untreated samples. Attenuated total reflectance infrared spectroscopy was used to study the chemical structure of the coatings.

### INTRODUCTION

In our work on water proofing certain types of porous cellulosic matrices, one of the requirements that had to be met was that the coatings be very thin in order that they would detract little from the bulk properties of the matrix itself. A low-pressure gas discharge method of polymer deposition was adapted to this purpose. The coating work reported here was done on a filter paper which represents one type of the porous cellulosic matrices studied.

The practical utilization of low-pressure discharge technique of polymer formation goes back to the work of Goodman.<sup>1,2</sup> Since that time, the technique has been widely explored by the capacitor, textile, container, and automobile industries in various protective coating applications. In the coating applications of paper, however, we find only one reference.<sup>3</sup> Coating of a paper between two electrodes in a glow discharge apparatus was claimed; however, no experimental results or the type of paper used were given. Thus, our application of the radiofrequency-discharged gases to coating of filter paper further illustrates the versatility of this technique.

### EXPERIMENTAL

#### Materials

The Whatman No. 1 (ash content 0.06%) filter paper disks (5.0 cm in diameter), dried at 60°C for 24 hr, were used as the coating substrates. The various monomers were used as received and were obtained from the following sources: styrene (Eastman Organic Chemicals, E), acrylonitrile

(E), 3-butenitrile (E), acetonitrile (E), toluene (E), benzene (E), p-xylene (E), methylene chloride (E), benzonitrile (E), chlorobenzene (E), 2-chloro-1-butene (Chemicals Procurement Labs., CPL), triethylsilane (CPL), *p*-nitrostyrene (K & K Laboratories, Inc.), vinyl chloride (Matheson Gas Products), isoprene (Monomer-Polymer Labs.), and hexane (J. T. Baker Lab. Chemicals). Helium, high purity grade, was obtained from Matheson Gas Products. du Pont Fiber Identification Stain No. 4 and staining chart were obtained by courtesy of the Dyes and Chemicals Division of Organic Chemicals Department, E. I. du Pont de Nemours & Company.

### Low-Pressure Plasma Generation

**Instrument.** The instrument used in this work was the LTA-600L Low Temperature Asher manufactured by Tracerlab, a division of Laboratory for Electronics, Inc. The instrument has five "ashing" (reaction) chambers (approximately  $6 \times 12$  cm large) which were modified by us (Fig. 1) so that the monomer vapors could be introduced into the chambers without being subjected to direct activation by the radiofrequency field. The rf generator operates at 13.56 MHz and delivers from 0 to 300 watts of continuously variable output power. The instrument was connected through a cold trap (Dry Ice/acetone) to a Welch Duo-Seal vacuum pump.

**Typical Coating Procedure.** The samples were placed either on a copper support in a horizontal position at the base of the excitation tubes (A) or in a vertical position in the reaction chambers about 2 cm beyond the junction of the excitation tubes. With the samples in place, the reaction chambers were generally evacuated to 0.10 mm pressure, and then helium

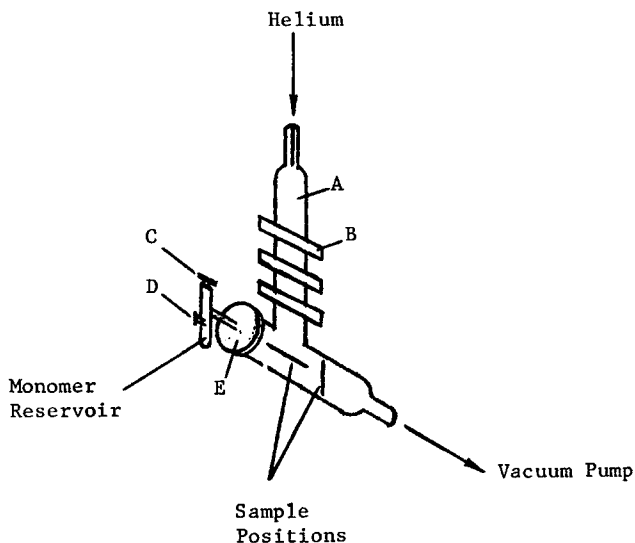


Fig. 1. Schematic representation of coating chamber.

was introduced at flow rates from 4 to 10 cc (STP)/min to achieve pressures of 0.15 to 0.20 mm. These pressures were obtained while the system was continuously pumped. Monomer was next added to the previously evacuated monomer reservoir through the rubber septum (D) by means of a hypodermic needle. The rf coil (B) was then activated at power outputs from 80 to 300 watts to transfer the radiofrequency energy into the flowing helium. The tuning circuit in the instrument was used to achieve a match between the impedance of the helium-filled excitation tube and the impedance of the generator and was adjusted until the reflected power was a minimum. This resulted in a helium plasma generation that glowed and filled the entire excitation tube, reaction chamber, and part of the vacuum line behind the reaction chamber. The monomer vapors were then admitted through the needle valve (C) on the chamber window (E) at a rate that barely quenched the helium plasma in the chamber. This resulted in the total gas pressure in the chamber of 0.40 to 0.85 mm, depending upon what the initial pressure was, what the monomer was, and the extent to which the helium plasma was quenched. Early in the work it was found that when the samples were placed upon a copper plate support of a size slightly larger than the sample itself, a more efficient coating deposition could be achieved. It should be emphasized that the copper plate is not a part of the electrical circuit of the instrument. In the experimental arrangement that we have used, little gas stream would be expected to go through the paper. Only one reaction chamber was used at a time, as it was difficult to monitor several at the same time.

Other variations in this procedure were also tried; for example, monomer vapor was used to adjust the pressure in the reaction chambers instead of helium before the rf coil was activated; a mixture of monomer vapors and helium was used in direct activation; and monomer vapors alone were used in the discharge. The indirect activation of monomer with discharged helium gave the best results in most cases. The maximum coating deposition rate occurred usually when the plasma glow was barely visible in the reaction chamber and the instrument was monitored and adjusted for a minimum of reflected power throughout the experiment.

### Characterization of the Water Vapor Barriers

**Water Vapor Permeability.** A modified Tappi Standard T 448 m-49 procedure was used in the determination of water vapor permeability of the coated filter paper samples. Water vapor permeability is defined in this test as the weight of water transmitted per unit time and per unit area. The open-mouthed cup was of such a size that it could be accommodated on the pan of an analytical balance, and it had a circular opening 2 in. in diameter. The samples, treated side down, were fitted between two circular aluminum disks of 1.5-in. diameter opening and were then attached to the cup by means of screw caps permanently fitted with a Neoprene gasket. The whole assembly, containing 30 ml of distilled water, was then weighed to four decimal places. The cups were placed in a standard

laboratory fume hood with an air circulation rate of 500 ft/min over the exposed surface of the samples. The assemblies were periodically weighed over a 20-hr period. The weight loss was found to be linear with time and is reported in units of  $\text{g}/\text{m}^2/24 \text{ hr}$ . Since the outside humidity was not controlled, each time a new series of tests was started a control was included. The large variation in the water vapor transmission of the controls was the result of a variation in the relative humidity from above 90% to below 40% on different days.

As the untreated filter paper discs (six samples) had practically identical water vapor transmissions, only one sample per series was used as the control. Exposing a sample to pump-out and styrene, toluene, or acetonitrile vapors for 5 min, without the plasma turned on, produced only minor (about 1%) variation in the water vapor transmission from that of the control.

**Attenuated Total Reflectance (ATR) Infrared Spectroscopy.** ATR infrared spectroscopic examination of all the coated sample surfaces was made on a Perkin-Elmer Infracord Model 237 using a Wilks Model 9 internal reflectance attachment and a Wilks reference beam attenuator. The KRS-5 crystal with  $45^\circ$  faces and an angle of incidence of  $60^\circ$  was used in the examination in the 2- to 16-micron range.

**Dry and Wet Tensile Breaking Strength.** Tensile breaking strength of the coated samples was determined in an Instron Model TM-M tensile tester at a speed of 0.5 cm/min. Two clamps 1 in. wide with the clamping surface in the plane parallel to the direction of motion were used to secure the samples. The samples were cut into  $0.5 \times 2$  in. strips which were conditioned at 50% relative humidity and  $70^\circ\text{F}$  ( $21^\circ\text{C}$ ) prior to testing. The wet tensile breaking strength was determined on samples that had been placed in distilled water for 10 min and then drawn.

**Coating Thickness and Staining Characteristics.** An indication of coating penetration was obtained by first staining the samples with du Pont Fiber Identification Stain No. 4, followed by microscopic examination of the cross section of thin slices of the stained samples.

The staining was done according to the suggested procedure. The coated samples were first immersed in hot water, followed by a boiling 1% water solution of du Pont Fiber Identification Stain No. 4, using approximately 10 ml of solution per sample. The sample was kept in the solution at the boil for 1 min, then removed, rinsed, and dried.

## RESULTS AND DISCUSSION

Of the 16 organic monomers coated on the Whatman filter paper, 14 gave coatings that functioned as water vapor barriers in various degrees. Two monomers, benzonitrile and *p*-nitrostyrene, gave coatings that did not possess water vapor barrier properties. All samples suffered some decrease in dry tensile strength upon coating; however, their wet tensile strengths were anywhere from 3 to 34 times that of the untreated samples.

In the following discussion, the various monomers have been divided into four groups: (1) aromatic hydrocarbons, (2) nitrile monomers, (3) chlorine-containing monomers, and (4) isoprene, triethylsilane, and hexane.

## Coating Deposition Efficiency

Some general observations regarding coating deposition efficiency may be made. First of all, depending upon the experimental parameters (pressure, flow rate, power level), most of the monomers could be converted into either oily deposits, dry powders, or nontacky coherent films. Variation in the experimental parameters available for depositing a nontacky film upon a cellulose substrate is considerably more limited than that for depositing a nontacky film upon a glass or a metal surface. The amount of coating deposited at a fixed pressure and power level is a function of time and, at a fixed pressure and time, a function of power level within certain limits depending upon the monomer used. In the case of filter paper as the substrate, a large scatter in the coated sample weights was always observed.

TABLE I  
Water Vapor Transmission of Whatman No. 1 Filter Paper  
Coated With Aromatic Hydrocarbons

Monomer	Pressure, mm		Power, watts	Time, min	Water vapor trans- mission, g/m <sup>2</sup> /24 hrs	Decrease, %
	Initial	Helium				
Control	—	—	—	—	229.7	—
Benzene	0.10	0.15	300	5	185.2	19.4
Benzene	0.10	0.15	200	5	198.9	13.5
Benzene	0.50	0.60	300	5	188.6	17.9
Control	—	—	—	—	219.5	—
Toluene	0.10	0.15	300	5	150.9	31.3
Toluene	0.50	0.60	300	5	195.5	11.0
Control	—	—	—	—	219.5	—
<i>p</i> -Xylene	0.10	0.15	150	10	157.7	28.2
<i>p</i> -Xylene	0.10	0.20	150	10	188.6	14.1
<i>p</i> -Xylene	0.10	0.50	200	5	212.6	3.2
Control	—	—	—	—	301.8	—
Styrene	0.50	0.60	300	5	225.3	25.4
Control	—	—	—	—	377.2	—
Styrene	0.10	0.15	300	5	257.2	31.9

This is probably due to the sensitivity of cellulose to dehydration and/or degradation by plasma as well as the hygroscopic nature of cellulose in general. Thus, no quantitative correlations are possible; and furthermore, to what extent an increase in the coated sample weight represents the coating weight cannot be easily determined.

**Aromatic Hydrocarbons.** Some of the experimental data on this group of monomers are recorded in Table I. The largest increase in sample weight from benzene, toluene, and styrene monomers was obtained by starting with low initial pressures ( $\sim 0.10$  mm) and at high power levels (300 watts). From *p*-xylene the largest increase was obtained by starting with low initial pressures and at a medium power level (150 watts). This

TABLE II  
Water Vapor Transmission of Whatman No. 1 Filter Paper  
Coated With Nitrile Monomers

Monomer	Pressure, mm		Power, watts	Time, min	Water Vapor trans- mission, g/m <sup>2</sup> /24 hr	Decrease, %
	Initial	Helium				
Control	—	—	—	—	287.4	—
Acetonitrile	0.10	0.20	300	5	202.3	29.7
Control	—	—	—	—	324.7	—
Acetonitrile	0.10	0.50	200	5	272.3	16.2
Acetonitrile	0.10	0.15	150	5	284.6	12.4
Control	—	—	—	—	377.2	—
Acrylonitrile	0.10	0.15	200	5	336.0	11.0
Control	—	—	—	—	504.0	—
3-Butenenitrile	0.10	0.15	100	5	480.0	4.8

TABLE III  
Water Vapor Transmission of Whatman No. 1 Filter Paper  
Coated With Chlorine-Containing Monomers

Monomer	Pressure, mm		Power, watts	Time, min	Water vapor trans- mission, g/m <sup>2</sup> /24 hr	Decrease, %
	Initial	Helium				
Control	—	—	—	—	287.4	—
Vinyl chloride	0.50	0.60	300	5	211.6	26.4
Vinyl chloride	0.50	0.60	200	5	226.3	21.3
Vinyl chloride <sup>a</sup>	0.10	0.15	300	10	233.2	18.9
Control	—	—	—	—	301.8	—
Vinyl chloride	0.10	0.15	200	5	276.7	8.4
Control	—	—	—	—	377.0	—
Methylene chloride <sup>a</sup>	0.10	0.15	200	5	311.0	17.6
Methylene chloride <sup>a</sup>	0.10	0.50	200	5	325.0	13.8
Methylene chloride	0.10	0.15	200	5	358.0	5.1
Control	—	—	—	—	219.5	—
Chlorobenzene	0.10	0.15	100	5	185.2	15.7
Chlorobenzene	0.50	0.60	80	10	192.0	12.6
Control	—	—	—	—	185.2	—
2-Chloro-1- butene	0.10	0.50	300	5	168.0	9.0

<sup>a</sup> Direct activation of monomer.

may be related to the two substituents (methyl groups) per benzene ring in xylene.

**Nitrile Monomers.** Pertinent data on this group of monomers are recorded in Table II. The significant difference between this group of monomers and the aromatic hydrocarbons was that, with everything else the same, the largest increase in sample weight could be gained only at low to medium power levels (100–200 watts). At the higher power levels (above 200 watts), considerable discoloration of the samples occurred and little weight gain could be achieved.

**Chlorine-Containing Monomers.** Some of the experimental data are recorded in Table III. In this group of monomers, the conditions for the largest increase in sample weight appeared to be different for each member

TABLE IV  
Water Vapor Transmission of Whatman No. 1 Filter Paper  
Coated With Isoprene, Triethylsilane, or Hexane

Monomer	Pressure, mm		Power, watts	Time, min	Water vapor transmission, g/m <sup>2</sup> /24 hr	Decrease, %
	Initial	Helium				
Control	—	—	—	—	241.7	—
Isoprene	0.5	0.6	200	5	212.6	12.1
Control	—	—	—	—	584.8	—
Triethylsilane	0.10	0.15	200	5	466.3	20.3
Triethylsilane	0.50	0.60	300	5	532.5	9.0
Triethylsilane	0.10	0.50	300	5	572.1	2.2
Control	—	—	—	—	290.0	—
Hexane <sup>a</sup>	0.10	0.15	200	5	240.7	19.7
Hexane	0.10	0.15	300	5	255.2	12.0

<sup>a</sup> Direct activation of monomer.

Aliphatic chloro-compounds required moderate to high power levels (200–300 watts), while chlorobenzene required low power level (80–100 watts). Vinyl chloride required higher (0.5 mm) starting pressure for best results while the other aliphatic compounds required low starting pressure, and chlorobenzene seemed to perform well at low and high starting pressures.

**Isoprene, Triethylsilane, and Hexane.** Pertinent experimental data are recorded in Table IV. The best weight gain for isoprene involved high initial pressures (0.5 mm) and medium to high power levels (200–300 watts); for triethylsilane, low initial pressure and medium power level (200 watts); and for hexane, low initial pressure and medium to high power levels.

### Water Vapor Permeability

**Aromatic Hydrocarbons.** Benzene, toluene, *p*-xylene, and styrene as a group of monomers gave the best water vapor barriers. Styrene and toluene were about the same in efficiency and led the list of all the other monomers investigated. In general, the water vapor barrier efficiency was a function of the treatment time. However, usually a time was reached (20 min) beyond which no further improvement could be gained, and actually with *p*-xylene, prolonged treatment deteriorated the barrier efficiency of the coating. This may be attributed to excessive crosslinking and, hence, embrittlement and mechanical break-up of the deposited coating. Similar results have been observed with other monomers upon glass and metal substrates in radiofrequency-discharged plasma.<sup>2,4</sup>

**Nitrile Monomers.** In general, except for acetonitrile, at the higher power levels (above 200 watts) poor coating formation resulted and no water vapor barrier properties were achieved. Of this group of monomers, acetonitrile produced the best barrier, which was only slightly less efficient than that of styrene and toluene. The efficiency of the nitrile monomer coatings as water vapor barriers decreased in the order of decreasing nitrile content in the monomers. The absence of water vapor barrier properties for benzonitrile and *p*-nitrostyrene coatings was unexpected in view of the aromatic hydrocarbon data. Concomitant oxidation of the coatings, resulting in a structure that is more soluble to water vapor, could account for such a behavior.

**Chlorine-Containing Monomers.** In this group of monomers, the water vapor barrier efficiency did not correlate with the chlorine content in the molecule. Vinyl chloride gave the best barrier in this group of monomers and was also the next best after the aromatic hydrocarbons and acetonitrile. One major difference in this group of monomers occurred with methylene chloride, which gave the better barriers when subjected to a direct activation by the rf field rather than the indirect activation by activated helium as was true for all of the other monomers. In the case of chlorobenzene, increasing the power level beyond about 100 watts produced coatings with poor or no barrier properties.

**Isoprene, Triethylsilane, and Hexane.** In this group of monomers, triethylsilane and hexane gave the better barriers, and these ranked just below vinyl chloride in the overall order. The coatings formed from the triethylsilane appeared to be stable in the presence of water vapors. This apparently was not the case with films formed from dichlorodimethylsilane, as they underwent hydrolysis and cracking at ambient atmospheric conditions.<sup>2</sup> In radiofrequency-discharged plasmas, apparently little difficulties are experienced in obtaining films from these monomers.<sup>4</sup>

**Chemical Structure of Polymer Coatings.** ATR infrared spectral analysis of the coatings was performed to gain some information about the chemical structure of the polymeric materials formed. In all cases, except the isoprene, triethylsilane, and hexane, absorption bands characteristic of the coatings were observed.



Styrene coating contained the three diagnostic absorptions at 910, 750, and 697  $\text{cm}^{-1}$  for polystyrene, and acrylonitrile coating contained a free nitrile absorption at 2250–2210  $\text{cm}^{-1}$  typical of polyacrylonitrile. Thus, with styrene and acrylonitrile polymerization through the vinyl group was observed. The coatings from the four aromatic monomers (styrene, benzonitrile, chlorobenzene, and benzene) contained two prominent absorptions at 750 and 697  $\text{cm}^{-1}$ , which indicated that the benzene rings were monosubstituted and therefore pendant from the aliphatic polymer chains. Similar observations have been made by Schuler et al.<sup>5</sup> and Kronick, Jesch, and Bloor.<sup>6</sup> Furthermore, these are distinctly different results from those of Swift et al.<sup>7</sup> and Stille et al.<sup>8</sup> in which the benzene rings were incorporated in the polymer as the *p*-phenylene units. Chlorobenzene in the process of coating formation also produced the most noticeable changes in certain of the characteristic pure cellulose absorptions: C—O stretching at 1050–1030  $\text{cm}^{-1}$ , antisymmetric in-phase ring stretching at 1110  $\text{cm}^{-1}$ , CH bending, OH in-plane bending, CH<sub>2</sub> wagging, and C=C were all drastically reduced, indicating extensive reactions at the anhydroglucose unit in the cellulose. In addition, both chlorobenzene and methylene chloride introduced a new absorption at 1720  $\text{cm}^{-1}$  which is characteristic of ester and/or keto carbonyl groups.<sup>9</sup> The chlorine liberated under the rf discharge conditions would be expected to be an energetic species and could have acted as an oxidizing (dehydrating) agent in the formation of keto groups. Chlorine in water at acidic pH has been used before as a non-specific oxidant of cellulose.<sup>10</sup> Only methylene chloride showed any absorptions in the characteristic carbon-halogen stretching region at 794  $\text{cm}^{-1}$ , which is typical for two or more chlorines substituted on the same carbon atom.<sup>9</sup> Both chlorobenzene and methylene chloride introduced another new absorption at 1260  $\text{cm}^{-1}$  which is tentatively assigned to a vinyl ether group.<sup>11</sup>

In the case of the discharge polymerization of nitrile monomers (acrylonitrile and acetonitrile), the polymerization reaction took place through the nitrile group (in addition to the vinyl group for the acrylonitrile) as judged from the absorption at 2185  $\text{cm}^{-1}$  (conjugated —C=N—) and the brown-colored coating formation due to extensive C=N conjugation. In connection with some of our other work, we have observed 2180–2190  $\text{cm}^{-1}$  absorption with many other nitrile monomers when polymerized in an rf discharge upon metal or glass substrates. One of the earliest reports of discharge polymerization through the nitrile groups that we are aware of is that of Deichert and Tobin.<sup>12</sup>

### Other Characteristics of the Coatings

In all cases, the materials were deposited as tack-free, adhesive, and flexible coatings that did not seem to peel off with rubbing. The surfaces possessed water and oil resistance as a drop of water or silicone oil did not permeate the coating in 6 hr while the control was permeated instantaneously. Hot benzene extraction of samples coated with polymer deposited

from styrene plasma for 3, 4, and 5 min yielded polystyrene in 2.1-, 1.2-, and 0.5-mg amounts, respectively. No soluble material could be extracted from a sample plasma treated for 10 min. Thus, increased coating time resulted in increasingly crosslinked and/or grafted material. The insolubilization of the initially soluble polymer deposited from styrene plasma upon metal electrodes has been studied in some detail by Denaro et al.<sup>13</sup>

Perhaps the most significant differences between the various coated (only on one side) and uncoated samples showed up in their wet tensile strengths. Samples coated with the monomers chlorobenzene, toluene, *p*-xylene, triethylsilane, and acetonitrile, were evaluated in more detail. The dry tensile strengths of these coated samples decreased anywhere from 15% to 50% of the untreated samples, which was 83.6 kg/cm<sup>2</sup>. This was expected mainly because of two factors: (1) dehydration of the sample in the plasma and (2) partial oxidation and/or degradation of the cellulose. The wet tensile strength of the coated samples, on the other hand, was anywhere from 3 to 34 times that of the untreated sample, which was 2.0 kg/cm<sup>2</sup>. The elongations to break did not exceed 3%.

The staining procedure that was used on the coated samples made it possible to observe visually under a microscope the apparent penetration of the coatings into the filter paper cross section. The coating penetration varied on the average from 5 to 25  $\mu$ .

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