

## Barrier Coatings on Cellulose Fiber Mat

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### Synopsis

Two techniques were used in the deposition of thin, pinhole-free vapor barriers upon a Kraft fiber mat without affecting its combustibility properties. One technique involved a collodion spray precoat followed by low pressure styrene plasma coating, and the other involved a collodion spray coating. In the formation of the above coatings, two functional steps are essential: (1) surface pore covering, and (2) nonporous barrier formation.

### INTRODUCTION

The purpose of the work described here is to apply pinhole-free water vapor and gas barriers upon Kraft fiber mat without affecting its combustibility properties. In the past, pinhole-free barriers on Kraft fiber mat were obtained only after a considerable quantity of the barrier material had been deposited on the substrate.<sup>1</sup> This seriously affected the porosity of the mat and as a result impaired its combustibility.

The best barrier property with a minimum of material will be obtained only if a nonporous coating is formed. Unless this is achieved first, polymers of inherently low water vapor permeability, used to make the coating, will have little practical importance. In the formation of such a barrier upon a porous substrate, we visualize two functional steps in the process: (1) surface pore covering, and (2) formation of the nonporous barrier layer. It is important to realize that the material applied in the surface pore covering may represent the major part of the coating and yet not necessarily produce an effective vapor barrier by itself. However, its role in the subsequent formation of an effective barrier cannot be overemphasized, as our work shows. If the combustibility properties of the cellulosic material are to be maintained, serious penetration of the barrier material into the pores of the substrate has to be avoided.

Three variables—type of coating material, thickness of the coating, and surface barrier layer formation—have been explored in this work. Both objectives, the very low water vapor transmission into the mat and its unimpaired combustibility, as measured by the heat of combustion, have been achieved.

## EXPERIMENTAL

### Materials

The Kraft fiber felted mats were obtained by courtesy of Dr. Jean P. Picard of Picatinny Arsenal. Styrene was obtained from Eastman Organic Chemicals and was used as received. The poly(vinylidene chloride) latex (45% solids) was obtained from Polysciences, Inc., and flexible collodion was obtained from Fisher Scientific Co. 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.

### Coating Procedures

#### *Conventional Coating Techniques*

Poly(vinylidene chloride) coating was formed by spreading 2.0 g of the as-received latex over the sample area (28 cm<sup>2</sup>) and allowing the coating to dry at ambient conditions, followed by vacuum oven drying at 40°C/16 hr.

The flexible collodion coating was formed from a one-to-one mixture of the as-received collodion and a 75:25 mixture, by volume, of diethyl ether and ethyl alcohol. A commercial paint sprayer was used as the collodion applicator at 35 psi of nitrogen pressure. The spray gun was held at a distance of 10 in. from the surface of vertically mounted sample, and the spray was applied by a rotatory motion around the periphery of the sample for 5-sec time periods. Each coating was allowed to dry at ambient conditions before the next was applied. The final drying was done in a vacuum oven at 50°C/1 hr. In the formation of the "thin" coating, which contained pinholes, a total of 28 sec of spraying time was used. For the pinhole-free "thick" coating, 40 sec of spraying time was used.

#### *Low Pressure Plasma Coating Technique*

**Instrument.** The rf plasma instrument was constructed from commercially available components. For the energy source, a radio-frequency transmitter, Heathkit Model DX60B, with a 90-watt input and a 55-60-watt output was used. The output was fed into a linear amplifier, Heathkit SB-200, having a 500-watt capacity. This was coupled to the tank coil through a Bendix coupler Model 262, 0.5-225 mc/sec. A tuning circuit, located between the tank coil and the coupler, was used to achieve a match between the impedance of the gas-filled reaction chamber tube and the impedance of the amplifier output. The tuning circuit was adjusted until the reflected power was minimum. At this point, the maximum power was transferred from the tank coil to the gas.

The reaction chamber was constructed in the shape of a standard bell jar, (see Fig. 1). The outside diameter of the bell jar was 12 in., the inside diameter 11 in., leaving a 1/2-in. distance between the walls. The outside wall

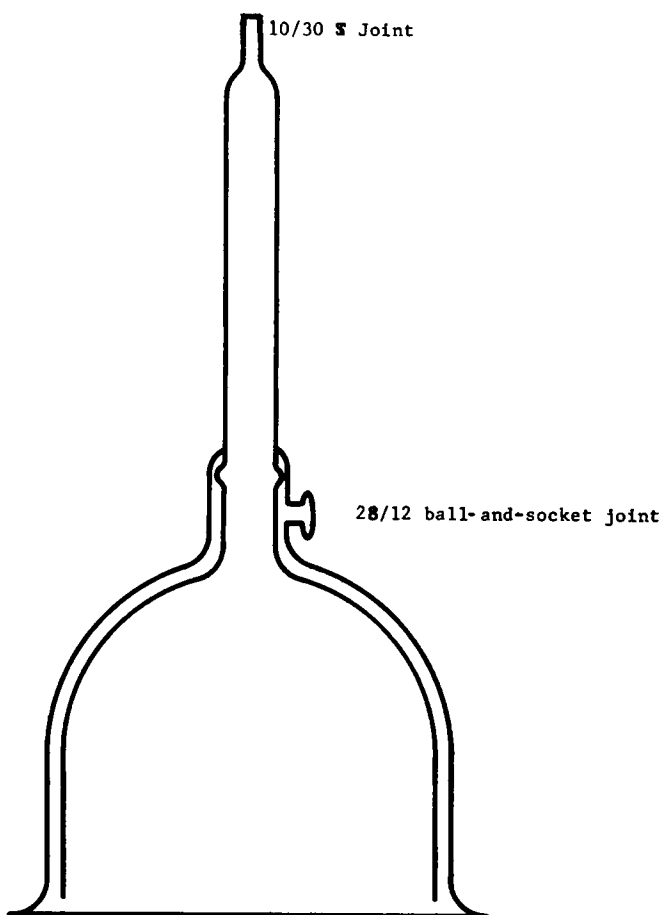


Fig. 1. Reaction chamber.

has an external opening at the top through a 28/12 ball-and-socket joint which leads to the vacuum pump. The inner and outer walls are attached at the top through a thick glass ring seal. Extending from the top of the ring seal is a tube 1 in. in diameter and 10 in. in length with a 10/30 joint at the top. The tank coil through which the radiofrequency energy is transferred to the gas fits around the 1-in. tube. The 10/30 joint is provided in order to allow different-size capillary tubes to be used inside the tube to conduct the flow of gas into the reaction chamber about 3 in. below the tank coil.

**Typical Coating Procedure.** The sample was placed on a glass support in a horizontal position centered under the excitation tube. The distance from the base of the excitation tube was varied depending upon the monomer and the geometry of the monomer capillary tube outlet. For optimum coating of styrene plasma, it was necessary to have the sample as close as possible to the base of the excitation tube. With the sample in place, the

reaction chamber was evacuated to 0.10 mm pressure or less. Helium was introduced at flow rates of 10–20 cc (STP)/min to achieve a pressure of 0.20 mm while the system was continuously pumped. The rf coil was then activated at a power output of 200 watts to transfer the radiofrequency energy into the flowing helium. This resulted in a helium plasma that glowed and filled the entire reaction chamber. The monomer vapors were then admitted through a needle valve and the capillary tube into the reaction chamber at a rate that barely quenched the plasma in the reaction chamber. This resulted in the total gas pressure of 0.40 mm. A minimum of 5 min of coating time was used.

### Heat of Combustion

The heat of combustion determinations were made on approximately 2-g samples by the Schwarzkopf Micronanalytical Laboratory, Woodside, New York.

### Gas and Vapor Permeability

Vacuum-type permeability measuring apparatus<sup>2</sup> was used in obtaining the gas flux of various gases. From such measurements one can determine whether the film is imperfection free and, if not, the extent of imperfections present.

### Coating Thickness

Attempts were made to determine the coating thickness by means of differential staining with du Pont Fiber Identification Stain No. 4 and microscopic examination of the cross section of thin slices of the stained samples. The staining procedure has been described before.<sup>3</sup>

## RESULTS AND DISCUSSION

### Gas and Vapor Permeability of Porous and Nonporous Films. General Considerations

The permeability of gases through paper of various kinds can be well represented by the relationship found for general consolidated and non-consolidated porous media. This applies also to the case of very tightly consolidated papers such as glassine paper.

The gas permeability coefficient  $K$  of a barrier can be defined as

$$J = K \frac{\Delta p}{\Delta X} \quad (1)$$

where  $J$  is the rate of gas flux per unit area of barrier,  $\Delta p$  is the pressure difference of gas across the barrier, and  $\Delta X$  is the thickness of the barrier. Thus defined,  $K$  for a porous medium can be expressed by the general expression.

$$K = B_0 \Delta p / \eta + K_0 \quad (2)$$

where  $B_0$  is a geometric factor of barrier,  $\eta$  is the viscosity of gas, and  $K_0$  is the Knudsen permeability coefficient. The Knudsen permeability  $K_0$  is proportional to  $T^{1/2}$  and  $M^{-1/2}$ , where  $T$  is the absolute temperature and  $M$  is the molecular weight of gas. Therefore,  $K_0$  or  $K$  measured at low pressure differential (for practical purposes) at a given temperature should follow the inverse proportionality to  $M^{1/2}$  of gases. In other words, a plot of  $K_0$  versus  $M^{1/2}$  yields a straight line passing through the origin.

On the other hand, the gas permeability of nonporous polymer film has a distinctly different dependence on the nature of the gas molecules and does not follow the relationship for a porous medium. In a homogeneous polymer film, the permeability of a gas is dependent upon the solubility and diffusivity of the gas and consequently less dependent upon the molecular weight of gases.

Another characteristic difference between transport through porous and nonporous polymer films is the selectivity of the permeant. The permeabilities of different gases to porous medium are relatively small, and, in the practical sense, nearly all gases permeate with about the same rate. This is not the case with nonporous polymer films. A simple functional relationship has been shown between the ratio of permeabilities of pairs of gases through polymer films. For instance, the permeability ratio of  $\text{CO}_2/\text{N}_2$  is approximately 25, and  $\text{O}_2/\text{N}_4$  is 4 for numerous polymers. On the other hand, the permeability ratio of  $\text{H}_2\text{O}/\text{N}_2$  varies over orders of magnitude depending upon the hydrophilicity of the polymer.

The measurement of water vapor permeability of both porous and nonporous barriers is much more difficult than the measurement of gas permeability due to some inherent properties of water itself. Some difficulties involved with water vapor permeability measurement are discussed by Yasuda and Stannett.<sup>2</sup> Therefore, the change of barrier property (from porous to nonporous structure) by treatment can be followed much more accurately by the measurement of gas permeabilities than by water vapor permeability measurements. As long as the medium is porous, water vapor permeability is nearly the same as the gas permeability, and the gas permeability provides more reliable data.

### Specific Coatings Obtained

Treatment of the Kraft fiber felted mat with a styrene or styrene/helium plasma at various partial pressures of styrene, various total pressures of the plasma, various rf power levels, and for various treatment times, produced a coating with only a marginal reduction in gas permeability (Table I). This occurred despite the fact that the mat was completely coated with polystyrene as the attenuated total reflectance infrared spectrum showed (Fig. 2). Thus, the large pore size of the mat did not permit the formation of a pinhole-free coating by this means.

Use of a 45% solids content vinylidene chloride latex to form a vapor barrier also resulted in a coating that was not pinhole free and in addition

TABLE I  
Gas Flux Measurements Q<sup>a</sup>

Sample	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub> ratio	H <sub>2</sub> O	He	H <sub>2</sub>
Untreated	$2.7 \times 10^{-2}$	$3.0 \times 10^{-3}$	0.9	$1.2 \times 10^{-3}$	$6.4 \times 10^{-2}$	$1.0 \times 10^{-1}$
Styrene plasma	$2.2 \times 10^{-2}$	$2.5 \times 10^{-2}$	0.9	—	$5.2 \times 10^{-2}$	$8.0 \times 10^{-2}$
VCl <sub>4</sub> <sup>b</sup> latex	$0.65 \times 10^{-2}$	$0.75 \times 10^{-2}$	0.9	$0.49 \times 10^{-2}$	$1.6 \times 10^{-2}$	$2.1 \times 10^{-1}$
"Thin" collodion	$3.9 \times 10^{-7}$	$3.0 \times 10^{-7}$	1.3	—	$6.5 \times 10^{-7}$	$8.5 \times 10^{-7}$
"Thin" collodion/styrene plasma	$1.4 \times 10^{-7}$	$0.088 \times 10^{-7}$	15.9	$0.93 \times 10^{-7}$	$0.92 \times 10^{-7}$	$1.0 \times 10^{-7}$
"Thick" collodion	$2.1 \times 10^{-7}$	$0.092 \times 10^{-7}$	22.8	$1.8 \times 10^{-7}$	$0.57 \times 10^{-7}$	$1.1 \times 10^{-7}$

<sup>a</sup> In units of cm<sup>3</sup> (STP)/cm<sup>2</sup>·sec·cm Hg; measurements made at  $\Delta p = 30$  mm Hg for gases and  $\Delta p = 10$  mm Hg for H<sub>2</sub>O.

<sup>b</sup> Vinylidene chloride.

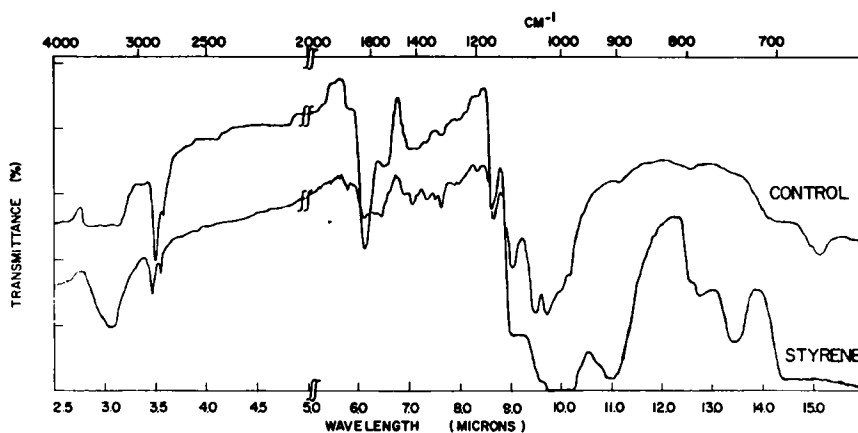


Fig. 2. ATR infrared spectrum of styrene/helium plasma-coated Kraft fiber felted mat.

impaired the combustibility characteristics of the mat. The heat of combustion data are listed in Table II.

Deposition of thin, pinhole-free coatings that did not impair the combustibility characteristics of the mats was achieved in two ways. One technique involved spray precoating on the mat with a solution of flexible collodion to give a "thin" coating and treatment of this coating with a styrene plasma for 5 min. The "thin" collodion precoating had some barrier properties but was not completely pinhole free. However, the plasma treatment converted it into a pinhole-free barrier with a  $\text{CO}_2/\text{N}_2$  ratio of 16. This is presumed to be due to simultaneous deposition and grafting of polystyrene upon the activated nitrocellulose surface. Similar observations on nitrocellulose films exposed to toluene glow discharge have been made by Kronick and Schafer,<sup>4</sup> and the decrease in permeability in their case was attributed to surface crosslinking.

A coating with equal barrier properties with a  $\text{CO}_2/\text{N}_2$  ratio of 22 could be obtained by simply depositing a "thicker" flexible collodion layer. This involved a total spraying time of 40 sec as compared to the 28 sec for the "thin" coating. The sample with the "thicker" coating, although still

TABLE II  
Heat of Combustion

Sample	Heat of combustion, Btu/lb
Untreated	5338
Styrene plasma	5604
$\text{VCl}_2$ latex	5276
"Thin" collodion	6156
"Thin" collodion/styrene plasma	5996
"Thick" collodion	5446

possessing heat of combustion properties somewhat better than those for the control, did not compare with those of the "thin" collodion/styrene plasma-coated material. Because of the rather loose nature of the mat, no easy sectioning and accurate determination of the coating thickness were possible. From the several observations that were attempted on the "thick" collodion-coated sample, the penetration of the coating material into the mat cross section appeared to be at least 50  $\mu$ .

The data in Tables I and II indicate that if more poly(vinylidene chloride) latex had been used in further attempts to decrease the water vapor permeability, the combustibility properties would have been further impaired. This study clearly demonstrates that water vapor barrier properties of a cellulosic mat can be improved without losing its characteristically high combustibility properties if two functional steps are observed: (1) surface pore coating, and (2) barrier layer formation.

The authors are indebted to Dr. A. Peterlin for the encouragement to complete this work; to Messrs. James Kearney, Oliver Bullock and Leon Pope and to Mrs. Carolyn Foust for their assistance. Partial support of this work by the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

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Received June 25, 1971

Revised August 2, 1971