

ABSTRACT

High density papers use extensively beaten chemical pulp. The paper therefore has a layered structure and closed surface with few large surface pores. Extrusion coating of these papers with polyethylene gives a structure with low oxygen and water vapor transmission rates. A similar improvement in gas barrier is now possible by coating the papers with aqueous, nonchlorine barrier polymer dispersions. Properties and grammage of the paper and coating are important. This technique offers an interesting alternative to conventional extrusion coating.

Application:

Coating high density paper with certain aqueous polymer dispersions provides equal barrier properties to extrusion coated products.

HIGH DENSITY (HD) PAPERS use extensively refined chemical pulp. Grease-proof paper is a “translucent machine-finished paper manufactured from wood pulp and hydrated to give grease and oil barrier” and “highly refined” with “excellent formation (1).” The fibers are fibrillated, swollen, and collapsed. This increases the contact area between fibers and fills many pores (2). The structure of the paper is layered and tortuous as **Fig. 1** shows. Calendering and surface sizing improve the barrier properties by increasing the paper density and closing the surface (3). **Figure 2** shows the closed surface of the same paper of **Fig. 1**.

Refining decreases the number of pores with a diameter of 0.1–5 μm . HD papers with a good grease barrier have few pores in this region. Void volume is 30%–35%, and average local density is 1000 kg/m^3 or higher. These values do not correlate with barrier properties and show

Polymer dispersion coated HD papers

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the importance of tortuous pore structure. Most porosity is due to large surface pores (4).

Because of the hydrophilic nature of cellulose, paper has poor resistance to water vapor. Dry cellophane—regenerated cellulose—does have a good oxygen barrier.

Extrusion coating of HD papers with polyethylene gives a structure with a low oxygen and water vapor transmission rate (WVTR) (3). Polyethylene film and HD paper have very limited oxygen barriers because of the structure of the polymer and the pores in the paper. Decrease in oxygen transmission rate (OTR) is probably due to sealing of pores in the paper surface (3, 5). The most important factors influencing OTR are refining of the furnish and calendering (3). The positive effect of high coating weight is due to improved contact between paper and coating, adhesion, compaction of substrate, coating thickness, and less coating defects (4). Good adhesion has a positive effect on gas barrier. The gas barrier of coated papers is partly due to change in the gas transmission mechanism.

Aqueous barrier polymer dispersions give paper or paperboard resistance to water, water vapor, and greases. The two primary groups of nonchlorine polymer dispersions are styrene-butadiene copolymers and various acrylates. Fillers, waxes, or both often modify dispersion coatings to improve barrier, friction, blocking resistance, economics, etc. These coatings are usually compostable and repulpable. They are

therefore more environmentally friendly compared with conventional extrusion coatings. Various off-machine coating and converting lines do the coating today. A trend exists for on-machine coaters with high volume products.

A similar effect of lower OTR is probably also possible with dispersion coated HD papers.

PROCEDURE

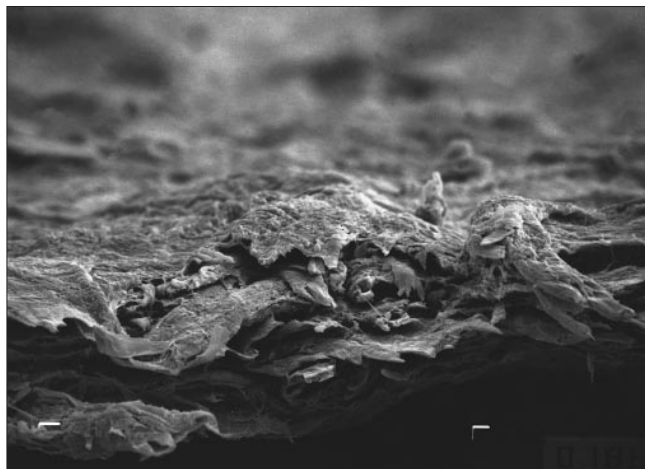
Materials

Although differences exist in the composition of HD paper grades and in surface sizing chemicals, they usually use moderately or highly beaten pulp. **Table I** shows the papers tested. One sample in our tests, 811, has less refining and fluorochemical surface treatment.

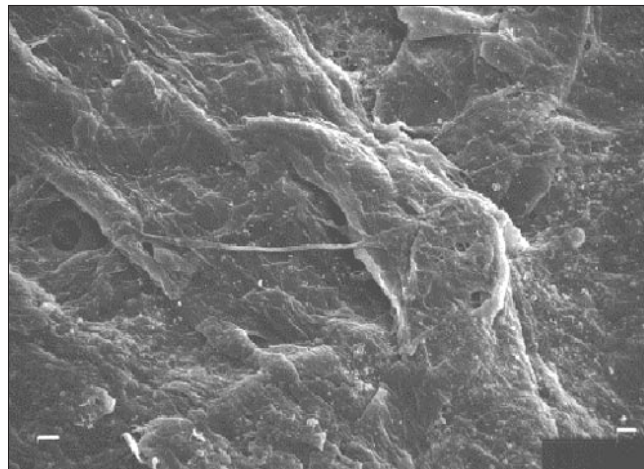
Coating was performed using a Mayer rod manually, a pilot coating line with a roll applicator and blade metering, or a production-scale coating line with roll applicator using rod metering. The test results also include a trial using a flexographic press. **Table II** shows the coatings tested.

Tests

WVTR measurement used flat samples according to a modified SCAN P22:68 method. Other similar standards are ASTM E-96 and DIN 53122. The desiccant is nonhydrous CaCl_2 that is on the bottom of an aluminum dish of specific size. Wax seals the sample tightly against the dish. As the water vapor penetrates the sample, the weight of the dish increases. After stabilization, the constant rate of weight increase is the WVTR expressed as $\text{g}/(\text{m}^2, \text{d})$. The



1. SEM photograph of HD paper cross section



2. SEM photograph of HD paper surface

results show the variable test conditions. The coating faced higher humidity.

OTR measurement used flat samples with OXTRAN from Mocon using standard ASTM D3985. Other conditions besides those in the standard were also used. Oxygen is led to one side of the sample and carrier gas takes the oxygen molecules that have penetrated through the sample to the sensor. A measurable voltage is created in the sensor. The working pressure of the sensor is higher than atmospheric pressure. The driving force for gas transmission is the partial pressure difference. Dry gases were used unless otherwise stated. The coated side was toward the carrier gas to avoid leakage. The measurement range was extended when needed by decreasing the measurement area or oxygen partial pressure. OTR values are in $\text{cm}^3/(\text{m}^2, \text{d}, \text{bar})$ with a partial oxygen pressure difference of 1 bar.

Water absorption tests used a Cobb tester with standards SCAN P12:64, ISO 535, and DIN 53132. The test measures the amount of water penetrated into the sample during a certain time. The measurement time is reported with the results, and results are in g/m^2 .

RESULTS

OTR

OTR of plain paper is several thousands $\text{cm}^3/(\text{m}^2, \text{d}, \text{bar})$ and is usually

not measurable. The effect of coating on OTR is obvious as Table III shows.

Coating was performed manually with Mayer rods except 828 that was a coating line. Coating weight refers to dry coating.

In the second series of Table IV, HD papers were coated with three different dispersions. Coating used Mayer rods. Samples were dried at 110°C for 20 s. Coating weight does not have a clear effect for 839. The OTR of this paper was below $4000 \text{ cm}^3/(\text{m}^2, \text{d}, \text{bar})$. This is very low for an uncoated paper. The probability of an interconnected pore system extending through the paper is higher for thin papers. As coating weight increases, the pores participating in the transmission become sealed and the number of coating defects decreases. Reaching the same OTR as with heavier papers is unlikely. For paper grades with a basis weight of $50 \text{ g}/\text{m}^2$, the values seem close to $60 \text{ g}/\text{m}^2$ with a variation in different grades. No difference between dry and humid gases was observable with the lowest coating weight of C. Opposite results indicate structural changes when using humid test gases.

A good OTR is also possible with dispersions containing no wax as Table V shows, although differences in WVTR were large as Table VI shows. OTR measurements used humid gases. Even unmodified latex

Designation	Basis weight, g/m^2
710	50
811	50
844	41
838	50
826	40
828	50
831	50
837	50
839	60

I. HD paper grades and basis weights

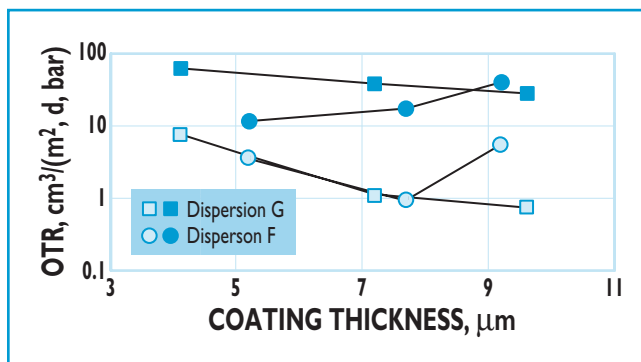
Designation	Description
A	Wax modified styrene-acrylate
B	Filled and wax modified styrene-acrylate
C	Wax modified styrene-butadiene with T_g of 8°C
D	Filled and wax modified styrene-butadiene
E	Styrene-butadiene with T_g of 20°C
F	Filled (50%) E
G	Filled (65%) E
H	Wax modified polyacrylate

II. Dispersions

gave the HD paper a low OTR. Increasing the oven setting to 130°C did not affect OTR with this dispersion. Good film formation is important. Other factors in coating such as metering and drying probably influence the OTR achieved in some

Paper	Coating	Coating weight, g/m ²	OTR, cm ³ /(m ² ,d,bar)
838	B	7	37
838	B	9	11
838	B	14	6
838	A	13	1.5
826	A	4	9.3
826	A	4 on both sides	<1
826	B	5	8
826	B	5 on both sides	4.4
828	A	7	15.6 (humid gases)
828	D	11	15.9 (humid gases)

III. OTR of dispersion coated HD papers



3. OTR as a function of apparent coating thickness for 828 with filled symbols indicating 50%–60% RH and empty symbols indicating dry test gases

cases due to coating structure and coating with paper interactions.

HD papers were coated on a pilot line using blade metering. Table VII shows the results indicating the role of the basestock. Differences between these and the previous results can be due to the drying conditions that gave different film formation. The applied web tension during coating and drying and the time before drying were different. Using blade metering also gives poorer coverage.

Figure 3 shows the effect of filling and coating weight with paper 828. Coating was performed with the pilot line and coating weight increased by multiple coating. Typical of these OTR measurements was a similar original increase. With humid test gases, the value kept increasing slowly indicating gradual changes in the structure. Reaching a stable value often took 24 h with the heavily filled samples. A big difference occurred with dry and humid gases in contrast with the previous results. Multiple coating and increasing coating weight improve OTR due to blocking of possible coating defects. Since coatings with different densities and barrier properties are under dis-

Paper	Coating	Coating weight, g/m ²	OTR, cm ³ /(m ² ,d,bar)
826	C	5	84 (humid gases)
826	C	5	87
826	C	7	46
826	C	11	7.1
844	C	6	11 (humid gases)
828	C	5	1.1 (humid gases)
831	C	7	0.9 (humid gases)
837	C	6	2.5 (humid gases)
839	C	7	0.3
839	C	12	0.3
839	C	15 total (both sides coated)	0.5
839	A	6	1.1
839	A	10	0.4
839	A	10 total (both sides coated)	1
839	H	9	0.5

IV. OTR of dispersion coated HD papers

Paper	Coating	Coating weight, g/m ²	OTR, cm ³ /(m ² ,d,bar)
828	C	5	1.1
828	C, 1/2 normal wax	6	0.94
828	C, no wax	7	0.89
838	Same dried at 130°C	7	0.96

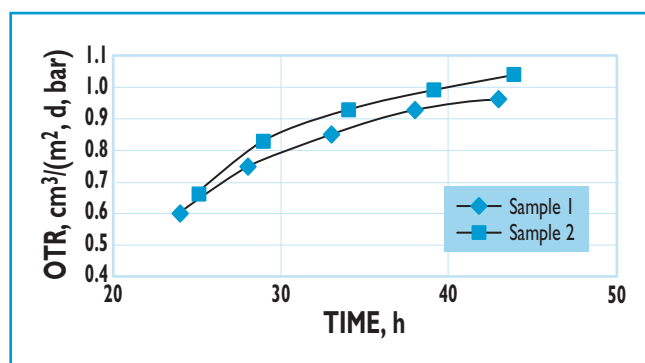
V. Effect of wax modification on OTR

Coating	Coating weight, g/m ²	WVTR	Cobb, 300 s
No wax	7	75	1.1
Half normal	6	2.6	0.4
C	6	1	0.1

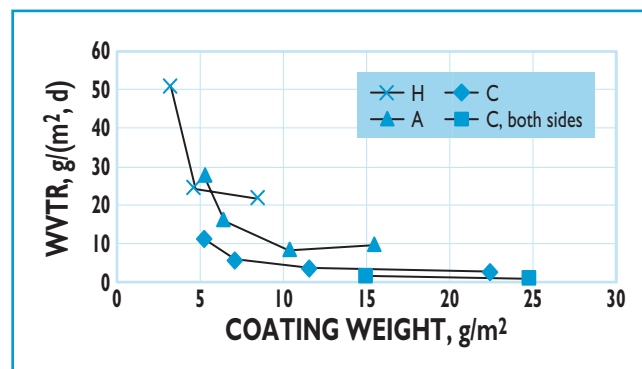
VI. Effect of wax addition on WVTR at 25°C and 74% RH and Cobb test for 5 min using 826

Paper	Coating	Structure	Coating weight, g/m ²	OTR
839	F	Twice one side	9	1.6
839	F	Once both sides	12	0.7
826	C	Once one side	4	206 (humid gases)
826	C	Once one side	5	11.4 (humid gases)
826	D	Twice one side	9	4.9 (humid gases)
828	C	Once one side	5	79.8 (humid gases)

VII. OTR of pilot coated HD papers



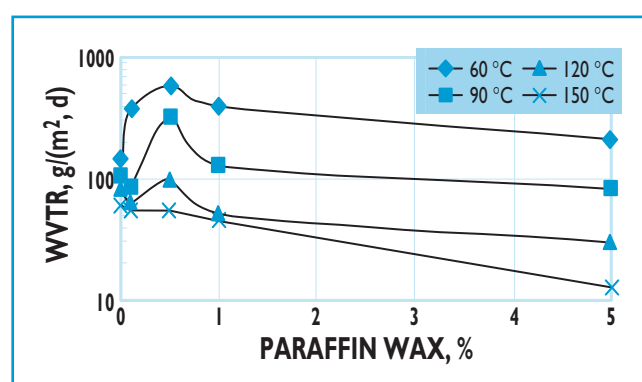
4. Increase of OTR when using humid test gases on samples coated on both sides



5. WVTR at 30°C and 95% RH as a function of coating weight on 839

Sample	Coating weight	WVTR, 75% RH, 25°C	OTR, cm³/(m²,d,bar)
Coated 710	2	138	1270
710 "water"	3.3	37.6	180 (dry) 143 (humid gases)
710, both sides	5.4	15.5	0.15 (dry) 1 (humid gases)
Coated 811	2.8	217	3020

VIII. Properties of samples coated using a flexographic press



6. Effect of oven temperature for 20 s and paraffin wax addition on WVTR at 25°C and 75% RH for coating weight 8–10 g/m² on 826

cussion, the proper comparison is barrier vs. coating thickness. Apparent coating thickness was calculated from the density and coating weight. OTR increased with temperature when measured with humid test gases. The carbon dioxide transmission rate was also very low.

Table VIII shows results with samples coated with C using a flexographic press. With humid gases, OTR was higher and an increase in OTR with time occurred as Fig. 4 shows. In this sense, OTR and WVTR are related. If WVTR is high or moderate, water vapor that has penetrated into the paper can increase OTR due to the highly hydrophilic nature of cellulose. WVTR of coated 811 is higher due to lower wettability of the surface. A large difference in OTR occurred with the paper grades due to different beating and coating with paper interactions. Closing of both surfaces gives a dramatic improvement in OTR. "Water" refers to a reverse side treatment with water to decrease a curling tendency.

The basis weight and properties of the paper have a strong effect on OTR of coated paper. Low basis weight could indicate higher contribution of z-direction pores on the permeability. Pores determine the OTR. Fibers are probably impermeable. The role of uniform coating without pinholes and close contact between paper and coating with little interfacial void volume become important. As paper basis weight increases, the tortuosity increases, and the role of the paper seems important. Fewer tortuous pores probably extend through the paper, and the

layered structure is thicker. Other factors such as changes in pore size distribution and void volume could also affect the results.

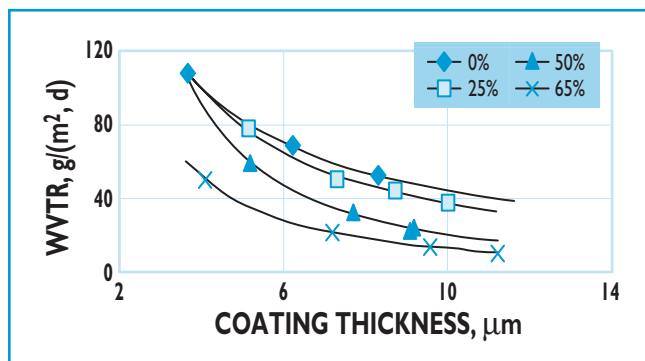
Some results in the literature indicate that extrusion coated kraft paper has a lower gas permeability than plain polyethylene film (6). A similar effect to that presented in this article occurs with other dispersion coated papers (4, 7), but the level of OTR is higher than with a coated HD paper of similar basis weight. This is due to pinholes and differences in pore structure—more and different types of pores due to lower level of refining.

WVTR

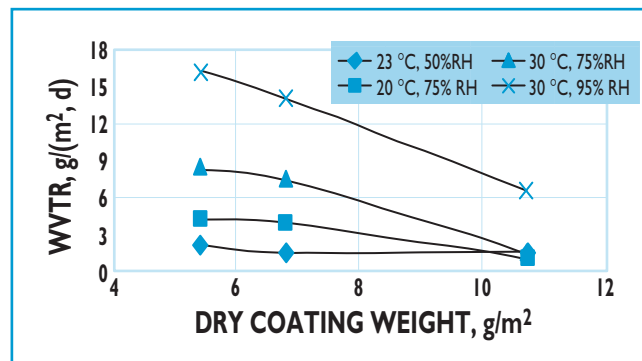
Uncoated HD papers have a high WVTR. WVTR is primarily a result of the degree of refining and different chemical treatments of the paper.

Figure 5 shows a comparison of WVTR as a function of coating weight of three dispersion coatings on 839 in "tropical" conditions of 30°C and 95% RH. Drying conditions were similar for all the coatings, and coating used Mayer rods. The effect of coating weight is obvious. These dispersions have the lowest WVTR.

Besides coating weight, drying and film formation are very important as Fig. 6 shows for dispersion E modified with paraffin wax. Dispersions usually contain fillers,



7. WVTR at 25 °C and 75% RH as a function of coating thickness and filling



8. WVTR in different test conditions as a function of coating weight using dispersion C on 826

waxes, or both. These have a clear influence on WVTR. Table VI presents the effect of wax addition in a styrene-butadiene dispersion. The effect depends strongly on the drying temperature and wax content (4). A thin layer of wax is probably the reason for the improved barrier properties by providing lower wetting and dissolution. Wax particles on the surface may also melt and bury the polymer (8). The effect of addition of plate-like fillers is evident in Fig. 7. A clear improvement occurs in WVTR as filler content increases in contrast with OTR values in Fig. 3. These results emphasize the role of a coating in the total WVTR performance of coated HD paper.

Figure 6 shows a comparison of WVTR as a function of coating

weight of C on 826 in different conditions. The behavior is similar. Proper test conditions are necessary or differences will be very small. Water vapor permeability increases with temperature. Good WVTR values are possible with dispersion coatings.

SUMMARY

Results indicate that dispersion coated HD papers can be excellent oxygen and water vapor barriers. Base paper and basis weight determine the level of OTR and influence the role of the coating. Higher paper basis weight gives lower OTR. The lowest OTR occurred with dispersions having the lowest WVTR. Coating modifications such as fillers and waxes are not necessary for low OTR

of dispersion coated HD papers. For WVTR, coating plays a major role. Modifications have a clearly positive effect on this barrier property. Proper film formation is important. Test results emphasize the possibility for using HD papers as a more environmentally friendly barrier layer in various packaging structures. **TJ**

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