



**IMPROVED PACKAGING MATERIALS MADE FROM BARRIER COATED PAPER
INCORPORATING VAPOR PHASE CORROSION INHIBITORS**

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ABSTRACT

Volatile Corrosion Inhibitors (VCIs) are used for safe and cost-effective protection of a wide range of metal articles. Cellulose based materials (paper and fiber board) are desirable packaging materials due to cost, material properties, and environmental attributes (bio-based content, recyclability), and these materials can be easily impregnated with VCIs to provide corrosion protection (e.g. for storage and transportation of metal parts). However, uses of these materials can be limited by the water affinity of paper/fiber board; and the highly porous nature which allow rapid depletion of the VCIs and exposure of the metal to corrosive elements in the surrounding atmosphere. The barrier properties of paper products can be greatly improved with wax or polyethylene coating, but such products are no longer suitable for recycling. Emulsion based coating products have also been used to improve the barrier properties of paper products. Unfortunately, many of these also reduce suitability for recycling. Some require multiple coats to achieve high barrier properties, thus increasing the product cost.

This paper presents studies with repulpable barrier coatings that are water-borne and applied in a single coating pass. When combined with VCIs, these provided recyclable packaging materials with excellent barrier properties and cost effective corrosion protection.

Key words: Volatile corrosion inhibitor, barrier, packaging, recyclable, coating

INTRODUCTION

Volatile Corrosion Inhibitors (VCIs) are a well-known and highly versatile range of products for the prevention of corrosion. VCIs can be delivered to the target metal in a variety of ways. One common product is paper sheeting impregnated with VCIs.¹ Unfortunately, the porous and hydrophilic nature of paper can limit the effectiveness of VCIs in protecting the target metal. Historically, polyethylene and wax coatings have been used to seal porous paper to provide a moisture barrier and/or moisture-vapor

barrier. These coatings also limit the migration of the VCI vapor away from the protected item, thus further improving the product effectiveness. While effective and relatively low cost, these coatings can render the paper non-recyclable, thus diminishing the otherwise positive environmental benefits of paper.^{1,2,3} Numerous alternate paper coating products are available to improve the barrier properties paper. Of these, water borne emulsion coatings are attractive based on cost, ease of application, and barrier attributes. Unfortunately many of these also have deficiencies such as: inferior barrier properties, loss of recyclability/repulpability, and/or the need for a primer coat before application of the barrier coat (thus increasing cost).^{2,4,5} In this paper, we report the development of an improved VCI impregnated paper with a barrier coating. The product is repulpable and recyclable. The coating is applied in a single coating pass. This paper further discusses some of the process variables necessary to achieve optimal coating performance.

EXPERIMENTAL PROCEDURE

Materials

Paper

40 lbs/3000 ft² (unit abbreviated as “#”) natural Kraft produced by Cascades[†] (East Angus, Quebec Mill). This corresponds to ~65 g/m²

Coatings tested

- A -Cortec[†] barrier coating
- B- Keim Additech[†] Ultraseal[†] W-954
- C- S-1601-L polyester based barrier coat
- D- S-1805-L barrier coating
- E –Resin Blend Formulation (based on DSM Neoresins[†] published formula U4-410)
- F- 1SR81A
- G - 1SR81B

Samples identified as C, D, F, and G were provided by SNP[†], Inc. , with the numbers corresponding to their product or experimental sample numbers.

All the above coating formulations are proprietary except for “E” above. The composition of coating E is shown below in Table 1.

Table 1
Formulation of Coating Composition E

ID	Additive	Weight %	Function
1	Proprietary acrylic/styrene copolymer emulsion	50	Binder
2	Proprietary acrylic/styrene copolymer emulsion	42.5	Binder
3	Proprietary nonionic wax emulsion	6	Water resistance
4	Proprietary polysiloxane copolymer emulsion (20% in solvent)	0.2	Defoamer
5	Proprietary acrylic copolymer emulsion	0.3	Thickener
6	2,4,7,9-tetramethyl-5-decyne-4,7-diol (50% in solvent)	1	Leveling agent

The formulation is based on a starting formula noted above, but with substitution of several of the indicated components with similar ingredients. The first three ingredients are the primary functional ingredients. These are: NeoCryl[†] A-1094 (1) and XK-87 (2), and Byk Cera[†] Aquacer[†] 498 (3). Formula E was prepared by mixing the listed ingredients until a homogeneous liquid was obtained.

[†] Tradenames

All other products were used as received, generally after stirring to make sure solutions/suspensions were uniform and representative.

Comparative Samples

A polycoated VCI paper product consisted of PE coated 40# Natural Kraft with 6# of polyethylene extrusion coated on one surface (produced by Plastic Coated Papers[†] Inc.), which had VCI solution applied to the non-polycoated side. The dried finished product is available as Cor-pak^{®†} VpCI^{®†} polycoated paper.

Commercial wax paper was obtained at a local grocery store.

Methods

Lab Coating

Samples were applied to 8.5 in x 11 in sheets of Kraft paper with Meyer rods (number 6 or 12) to achieve approximate targeted coating weight. Coated samples were immediately dried in a forced air oven at 40 °C for 5 minutes. The coated paper was then trimmed 7 in x 8 in to remove edges and uncoated regions. These trimmed samples were further dried for 5 min at 110 °C in forced air oven to obtain a dry weight. The weight of a dried uncoated paper sample was subtracted to estimate dry coat weight.

Pilot Production Coating

For pilot coating, the selected coating was applied by roll transfer which was metered by use of an air knife. The coating was dried by means of in-line oven sections to a final moisture content of ~ 6%. Line speed was approximately 400 ft/min. The final VCI containing product was first coated on one side with the barrier coating. The VCI was applied to the alternate side in a second coating pass. The VCI additive is a proprietary formulation containing ~20% active ingredients and 80% water.

Coating Uniformity

The presence of pinholes, uncoated streaks, or other defects in the surface coating was determined by applying corn oil to the coated surface. Approximately 1-3 drops were applied to the surface. This was spread evenly with a tissue to coat an area approximately 10 cm on a side. The presence of coating holes/defects became visible within about 1 minute, as the oil passed through the holes and became visible as dark spots in the paper.

Water Holdout

Water hold out was screened by applying drops of water to the coating surface.

Water Vapor Transport (WVTR)

WVTR was determined by a modified version of ASTM⁽¹⁾ E-96.⁶ Disks of the coated paper were clamped in machined aluminum cells. A rubber gasket provided a seal around the edges. The cells were filled with freshly regenerated silica gel. Filled cells were weighed at the start and periodically over a period of time from 1-2 days. The cells were placed in a chamber at ~73 °F (23 °C) and 50% relative Humidity. Due to modification relative to the official method, the absolute results may differ from those run according to the official method. However, results were found to be highly repeatable, and should provide reliable relative values for comparison of the different coating treatments.

As a check, two samples were tested for WVTR at a commercial testing lab (IPS Testing[†], Appleton Wi.) per the official method, and found to be in good agreement with the results as measured by the modified method.

[†] Tradenames

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959

Oil/grease resistance

Samples were tested for grease resistance (oil/grease resistance test) with the use of the 3M[†] test kit per Tappi⁽¹⁾ method T559.⁷ Samples were further tested by placing a drop of corn oil on the surface and watching for any signs of penetration into the paper.

Repulpability

Repulpability was initially assessed with an in-house method. Briefly, an 8.5 x 5.5 inch sheet of the coated paper was cut into ~1 inch squares. Approximately 200 mL of 170 °F (77 °C) water was placed in a blender and the blender was turned on. The squares were added (through the lid port) while the blender continued to run. An additional ~100 mL of 170 °F water (300 ml of water in total) was added and the blender allowed to run for a total of 30 seconds. The resulting slurry was poured into a shallow tray to examine for the extent of fiber liberation, in comparison to an uncoated paper sample. The final material (overall best performance) was tested at the above mentioned commercial testing lab according to the FBA⁽²⁾ method for repulpability.⁸ This method was designed to test recyclability of fibreboard, but has become the de facto standard method for assessing recyclability of other paper fiber based substrates.

VIA – Corrosion Inhibition Test

This testing was performed by standard methods as previously described.¹ In brief, sanded carbon steel plugs are suspended from a modified lid in a quart jar. Strips of the test substrate (1 in x 6 in) are hung from the inside of the lid, being sure they do not come in contact with the plug. The lids are screwed on tight and the jars are left to condition for 20 hours at ambient temperature. After conditioning, a glycerol/water solution is added to the jars to accelerate corrosion and left to sit at ambient temperature for two hours, then in a 40°C oven for two hours. The plugs are removed and rated on a scale of 0 (heavily corroded) - 3 (no visible corrosion). A grade of 2 or 3 is considered passing.

Razor Blade – Corrosion Inhibition Test

This testing was performed by standard methods as previously described.¹ In brief, carbon steel panels, are cleaned in methanol and dried. Two drops of deionized (DI) water are placed on the metal panel and covered with the substrate of interest. After two hours, the substrate is removed and the panels inspected. Panels with any sign of corrosion, pitting or staining are deemed to “fail” the test. A second test is conducted with copper panels. The method is the same except that a 0.005% sodium chloride solution is used instead of water and the test time is extended to 4 hours.

RESULTS

Lab Coated Samples

Based on manufacturer information and previous experience, it was expected that a dry coating weight of 6-12 # would be sufficient to achieve a uniform (defect free) surface coating with barrier properties in the desired range. Given the solids content of the materials, number 6 and number 12 meyer rods were used to apply the coating solutions as described in the methods section. Samples were tested for WVTR. The results for coating weight and WVTR are shown in Table 2.

[†] Tradenames

⁽¹⁾ TAPPI 15 Technology Parkway South, Suite 115, Peachtree Corners, GA 30092

⁽²⁾ Fibre Box Association (FBA):25 Northwest Point Blvd. Suite 510,Elk Grove Village, IL 60007

**Table 2:
Coating weights and WVTR results**

Coating ID	Meyer Rod	coating solids fraction	Lbs/3000 ft ² . (g/m ²)			WVTR* g/(m ² *d)
			Dry Weight Coated	Net Weight Coating	Predicted Coat Wt.	
A	12	0.56	51.2 (83.3)	11.6 (18.8)	9.4 (15.4)	13
B	6	0.45	45.6 (74.2)	6.2 (10.0)	3.8 (6.2)	58
B	12	0.45	46.9 (76.4)	7.2 (11.8)	7.6 (12.3)	57
C	6	0.4	46.8 (76.1)	6.8 (11.0)	3.4 (5.5)	57
C	12	0.4	47.1 (76.7)	7.6 (12.3)	6.7 (11.0)	42
D	6	0.53	47.6 (77.5)	8.1 (13.2)	4.5 (7.3)	39
D	12	0.53	48.6 (79.2)	9.2 (15.0)	8.9 (14.5)	29
E	6	0.47	47.6 (77.5)	7.5 (12.2)	4.0 (6.4)	11
E	12	0.47	48.5 (78.9)	8.6 (14.0)	7.9 (12.9)	11
F	12	0.53	47.4 (77.1)	8.1 (13.2)	8.9 (14.5)	26
G	12	0.53	48.4 (78.8)	9.1 (14.9)	8.9 (14.5)	32

*WVTR measured at 50% RH 73 °F (23 °C)

The coating weights were approximately as predicted with use of the number 12 coating rods. Application with the number 6 rods resulted in coating weights not greatly different from the number 12 rods. This may be due to the viscosity and flow properties of the coating solutions, which prevented the formation of a thinner coating layer. Based on the above, a number 12 rod was used for preparation of all subsequent lab coated samples. By observation, formula A had a higher viscosity than the other formulations. For high barrier coatings (WVTR < 20 g/(m²*d)), WVTR differences between samples of less than ± 3 are not considered to be significant (based on observed variation in test results). For samples with higher WVTR values, the variability of results tends to be greater.

On inspection with oil, all samples (used in the WVTR test) showed good coating uniformity and an absence of (or very small number of) pin-holes. Therefore, it was concluded that the WVTR results were reasonably representative of the coating barrier properties, and not artifacts due to sample defects.

Samples were tested for water holdout as described above. With all materials, the drops beaded up and no absorption of water was observed even after several minutes.

All samples were also tested for oil/grease resistances as described above. All the coatings obtained a rating of 12 with the oil/grease resistance test, when tested on a portion of the sample free from mechanical coating defects (e.g. pinholes). Tests with a drop of corn oil produced the same results, with no absorption or penetration of oil.

The four materials with the best WVTR values (A, E, F, and G) were forwarded on for additional testing. These were subject to the in-house test for repulpability as described in the methods section. Of these, materials A, F, and G showed repulpability comparable to the uncoated paper stock. Material E had remaining fragments of unpulped material, in sizes up to about 6 mm (in longest dimension). Of the 3 materials with acceptable repulpability, material A had the best WVTR values and was selected for further testing.

Pilot Coating

Samples of the base paper coated with material A were prepared on the commercial coating line as described in the method section. Coat weight, solution solids content, and operating parameters were adjusted until the resulting coated product was substantially free of coating defects (streaks or pinholes as detected by application of vegetable oil to the surface). The resulting one-side coated (C1S) material was tested for WVTR, water and oil resistance. The C1S material was then put through the coating process a second time to apply VCI to the other side (to make the C2S material). The C2S product was tested again for WVTR. It was also subject to the standard corrosion inhibiting tests (VIA, steel razor blade, copper razor blade), and received a passing score on all tests.

The WVTR results of the C1S and C2S products, along with some comparison materials, are shown in Table 3.

**Table 3:
Coating weight and WVTR of production and comparative samples**

Coating	Lbs/3000 ft ² . (g/m ²)		Mils (micron)	WVTR** g/(m ² *d)
	Dry Weight	Net Weight	Thickness	
	Coated	Coating*		
C1S	50.8 (82.7)	10.8 (17.6)	4.8 (118.8)	19
C2S	54.3 (88.4)	14.3 (23.3)	4.8 (118.8)	16
Polycoated	59.6 (97.0)	19.6 (31.9)	5.3 (131.3)	17
Waxed paper	19.2 (31.3)		1.3 (32.5)	163

* Coating weight includes barrier coating and VCI for C2S and Polycoated

**WVTR measured at 73 °F (23 °C), 50% RH

CONCLUSIONS

It is shown by the data presented in the paper that it is feasible to produce repulpable VCI paper with water vapor barrier properties very close to that of polycoated paper, and much better than a commercial waxed paper. Further these are produced by application of a single coat of water borne coating solution, making them cost competitive with polycoated. It is expected that with further optimization of the coating formulations, the barrier properties could be further improved to be equal to or even superior to those of polycoated paper. While there appeared to be distinct differences in WVTR properties of the specific formulations, obtaining a defect free continuous coating was critical to high WVTR performance. The viscosity of formula A was higher than the others and may have been a significant factor in achieving the desired coating uniformity under industrial coating conditions.

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