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MODERN ADVANCES IN ENVIRONMENTALLY FRIENDLY VAPOR-PHASE CORROSION INHIBITING COATINGS: EXPANDING THE REALM OF VpCI PACKAGING

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ABSTRACT

Coatings for substrates used in the packaging industry have recently undergone a substantial transformation with the push to promote environmentally friendly or “green” products. This distinct change of direction has transcended from non-renewable materials derived from fossil fuels which are pollutants to bio-based renewable-resource-derived products which, in comparison, drastically reduce greenhouse gas emissions and hazardous waste. This shift has already been witnessed in the food packaging industry and now the automotive, cosmetic and other packaging industries are following in its path. This paper discusses the advancement of environmentally friendly VpCI-containing coatings that have allowed for the development of novel VpCI packaging products. The products discussed include grease resistant and water resistant papers, cohesive film, anti-skid linerboard, and masking film. Each of these products is environmentally friendly having been constructed from non-hazardous, water-based coatings, which in some cases provided biodegradable and bio-based products. In addition to their unique physical properties each of these products provides excellent multi-metal corrosion protection. Test methods employed in assessing the performance of the materials will be discussed including physical properties, as well as contact-, barrier- and vapor-phase corrosion inhibiting abilities. The advantages provided using these products will be demonstrated through real-life field applications.

Keywords: Vapor-phase corrosion inhibitor, packaging, environmentally friendly, grease resistant, water resistant, cohesive film, masking film, anti-skid linerboard

INTRODUCTION

Vapor-phase corrosion inhibiting (VpCI) packaging products have become widely used to protect metal parts from corroding during shipment and storage. Advances in the corrosion inhibitors used within these products have allowed for the elimination of toxic and hazardous compounds including nitrites, dicyclohexylammonium nitrite (DICHAN), and chromates, among others, while providing the same or better levels of corrosion inhibition. Furthermore, the use of solvent-free, aqueous coating solutions results in a less hazardous coating process. Combining this chemistry with water-based binders and adhesives has resulted in the development of novel corrosion-inhibiting flexible packaging products with varying physical properties. Examples discussed herein include grease and water resistant corrosion inhibiting papers, VpCI cohesive film, VpCI anti-skid linerboard, and VpCI masking film.

Expanding the use of paper-based packaging products and the development of environmentally friendly water-based coatings for paper provides a sustainable packaging alternative to petrochemical based products. Grease and water resistant corrosion inhibiting papers are two good examples of multi-purpose packaging products which can be produced using environmentally friendly products. Grease resistant papers are quite often based on perfluorochemicals (PFCs) or wax-based products, both of which have adverse environmental impacts. Traditional waxed papers are not repulpable which contributes to environmental issues and increased waste. Products based on PFCs have received much scrutiny and are believed to leach chemicals into the environment. Global distribution of these contaminants have been found in drinking water,[1,2] rivers and lakes,[3,4] and even animal blood and tissue.[5,6] Due to their biopersistence, statewide banning of these products is currently under review.[7] Abstaining from these traditional coatings, the use of water-based emulsions in combination with natural co-binders has allowed for the development of a bio-based and biodegradable grease resistant paper which is also 100% recyclable and repulpable. The grease resistant paper provides corrosion protection for oiled or dry parts during storage, transit or overseas shipment. When used to protect oiled parts, the barrier coating leaves the oil captive on the metal surface instead of absorbing it, keeping the parts protected. The paper also provides protection against incidental exposure to oils, greases and solvents. Particular applications where this paper would be beneficial include the protection of greased bearings, pump housings and gear boxes.

Likewise, moisture barrier papers have been produced utilizing similar green chemistry strategies, providing an alternative to traditional waxed and polycoated products. The moisture barrier protects metal parts from exposure to water and moisture-vapor while protecting them from corrosion; which provides the extra protection necessary in cases of incidental contact and, more importantly, when parts are stored or shipped in areas of high and varying humidity. As a result of the coating chemistry used for this application, the final product is 100% repulpable and recyclable unlike conventional waxed or polycoated alternatives.

Although paper products are more sustainable than some of their counterparts, there exists many packaging applications where paper is not suitable and more durable materials such as films must be used. Recent advances and developments in bio-based and biodegradable polymers have helped to ease the reliance on petrochemicals and reduce the carbon footprint. Current research efforts have expanded the technology to produce a number of various bio-based polymers, including those based on polylactic acid, polyhydroxyalkanoates, starch, and sugars, among others. These advances in new methods for producing polymeric materials have expanded their availability as well as lowered their cost. Perhaps more importantly though is the advancement in physical and mechanical properties which are crucial to their integration into traditional polymer applications. In applications where petrochemical based materials must be used, either due to economic reasons or availability, achieving functional properties through water-based coatings in place of solvent-based products aids in the reduction of hazardous waste. Both of these approaches have been taken to produce adhesive films with varying properties including VpCI masking film and VpCI cohesive film discussed herein.

An environmentally friendly VpCI cohesive film that will bond only to itself, and not the metal parts wrapped within, has been developed and provides another option for packaging applications. In addition to aqueous corrosion inhibitors, the coating chemistry contains natural rubber latex derived from rubber trees as opposed to most synthetic rubbers which are produced from petroleum derivatives. The functional polymer used can therefore be considered bio-based and provides a renewable aspect that is not found with traditional petroleum based products. The application of this coating to both traditional and bio-based film substrates provides protection from corrosion and mechanical damage all in one. This product can be used in automated cold seal machines, is transparent, which allows for easy inspection, and is puncture resistant, resulting in a novel packaging product for corrosion protection. Since the film adheres to itself, it doesn't leave any residue behind, allowing the parts packaged within to be ready for use and corrosion free.

Another example of a functional packaging material constructed from non-hazardous materials is an anti-skid linerboard. This paper is used to prevent slippage of stacked products during shipment and storage and the addition of VpCIs offers corrosion protection. Unlike some traditional anti-skid papers, the coating applied does not cause harmful dust production or accumulation. When used in palletizing, the linerboard not only provides protection against accidental slippage, but also acts as a barrier between metal parts and the wood pallet itself, which often times acts as a source for corrosion.

Incorporating VpCI chemistries into a water-based pressure sensitive adhesive provides a non-hazardous coating solution for both traditional and modern films. Using a water based acrylic adhesive rather than a solvent based product has several environmental and safety advantages including, but not limited to, reduced exposure for workers, non-flammability, and reduction in hazardous waste. The masking film provides corrosion protection, while protecting metal surfaces from mechanical damage (scratching, marring). This product is often found in automotive applications to protect metal parts before and during assembly. Less known but pertinent applications can be found in processes of etching, plating, powder coating, sand blasting, flame spraying and thermal spraying. Traditional masking films are commonly used to protect new appliances, but do not contain VpCI; therefore, the integration of these additives into the product has expanded its application range and potential.

EXPERIMENTAL PROCEDURES

The performance of the grease-resistant paper was assessed via TAPPI T454[8] and the 3M Scotchban Test Kit. Although the 3M test kit was designed to test PFC based products, it provides a good measure for grease and solvent resistance and has been adapted under TAPPI UM 557[9] and TAPPI T559.[9] The test is comprised of twelve different test solutions which vary in aggressiveness as the composition ratios of castor oil, toluene and heptane vary. The solutions range from 100% castor oil to a 45/55 blend of toluene and heptane, respectively. The test is conducted by applying a drop of test solution to the substrate and waiting 15 seconds, after which the excess fluid is removed and the area examined for damage. Failure is indicated by darkening of the substrate caused by penetration. The procedure is repeated and the highest numbered solution that stands on the surface without causing failure is reported as the kit rating. The second test method used, TAPPI T454,[8] gives an accelerated comparison of the relative rates at which oils or greases may be expected to penetrate papers. Substrates are tested by placing 5 g of sand in a uniform pile and saturating it with 1.1 mL of colored turpentine solution. The substrates are placed on top of white book paper to allow for easy indication of staining beneath the substrate, indicating penetration. The results are reported as the time elapsed from addition of turpentine to the first sign of staining of the book paper. If staining has not occurred within 30 minutes, the test is terminated and reported as 1800+ seconds.

In order to assess the performance of the water resistant paper, traditional tests were conducted including water absorptiveness (Cobb test) and water-vapor transmission rate (WVTR). WVTR is a measure of the passage of water vapor through a substrate. The WVTR testing was conducted according to a standard procedure[10] by an accredited testing facility. The Cobb test[11] determines the amount of water absorbed by the substrate within a specified time. The test is carried out by placing the substrate in the test holder and clamping it down with a neoprene gasket to form a tight seal. Water (100 mL) is then placed on top of the substrate and after the specified time has elapsed the excess water is poured off. The substrate is then removed from the holder and sandwiched between two sheets of blotting paper. The surplus water is removed by moving a 10 kg roller over the sheet in two strokes, once forward and once back. The substrate is then weighed and the amount of liquid absorbed determined by the difference before and after. This value gets converted to give the amount of water absorbed in g/m^2 by multiplying by 100.

The performance of the VpCI cohesive film can be assessed through peel resistance and shelf life stability. Peel resistance is tested in accordance with ASTM D1876[12] and determines the relative peel resistance of adhesive bonds between flexible adherends. This test method is conducted by cutting 1 inch by 4 inch wide test strips which are bonded end to end in a string. The ends of the film are then attached to an Instron tensile tester and the value is recorded when peeling of the cohesive layers are observed. Shelf life determination is conducted according to the GM shelf life test[13] for cohesive films. This test involves sealing an arbitrary part within a pouch of the cohesive material such that three inches of cohesive layer are exposed on all sides. The pouch is then exposed to elevated temperatures and relative humidity for seven days. Any deterioration of the adhered layers is cause for failure.

The coefficient of friction (COF) for the anti-skid linerboard was determined by an outside facility in accordance with ASTM D1894.[14] This test method determines the coefficients of starting and sliding friction of the test substrate over itself as well as other materials such as metal. The test employs a 2.5" x 2.5" 200 gram sled pulled at a speed of 11.8 in/min and the COF is calculated as described in Equation 1.

$$\text{COF} = \frac{\text{Force to cause sliding of substrate (grams force)}}{\text{Sled weight (grams force)}} \qquad (1)$$

Properties of interest for a VpCI masking film include tack, peel adhesion and unwind force of the roll. The tack is measured according to ASTM D3121.[15] This test apparatus involves a small ramp with a 2-9/16" incline at a 21-30° angle and a distance of 7" (Figure 1). A steel ball, measuring 1" in diameter and 20 grams, is released from the top the ramp and rolls over the adhesive substrate of interest. The time to travel across a given distance over the substrate is then recorded. The test is conducted in triplicate and the results averaged and the value compared to a non-masking film used as the control. Peel adhesion is tested according to ASTM D3330[16] and demonstrates the relative bond strength of an adhesive substrate to various surfaces. The test method gives a measure of adherence, when peeled at a 180° angle, to a standard steel panel (or other material surfaces). The force required to unwind a roll of pressure sensitive tape, the unwind force, is assessed via ASTM D3811.[17] This test method involves pulling the loose end off the roll roughly six inches using an Instron tester and the required force to do so is recorded.

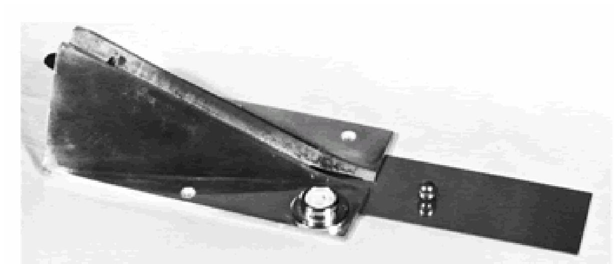

FIGURE 1 - Tack Test Apparatus[18]

Although the functional properties tests are unique for each product discussed, the corrosion inhibition tests are generally applicable to all packaging products. To fully evaluate corrosion inhibition three different tests are conducted to assess the contact-, barrier- and vapor-phase corrosion inhibiting abilities. Contact-phase corrosion inhibition testing is performed according to the Razor Blade test[19] and is carried out as follows: Carbon steel panels, constructed of CRS SAE 1008/1010, 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 for any sign of corrosion, pitting or staining. This test can be adapted to other metals such as copper, galvanized steel or aluminum with a slight modification in the test solution used for each metal (0.005% sodium chloride, 3.5% sodium acetate or 3.5% sodium chloride respectively) and the exposure time.

Barrier-phase corrosion inhibition is tested according to the SO_2 Test[20] which evaluates the substrate's performance as a barrier against an aggressive sulfur dioxide (SO_2) environment. The test is conducted by wrapping carbon steel panels within the substrate and allowing them to condition in a gallon jar for 20 hours at ambient temperature. After pre-conditioning the panels, an SO_2 gas environment is created within the jar and the wrapped panels are exposed to this environment at elevated temperatures (50°C) for 16 hours followed by room temperature for 8 hours in a cycling oven. The jars are then removed from the oven, panels unwrapped and visually inspected for any sign of corrosion. The panels are graded on a scale from 0 to 4, where grade 0 is heavily corroded (covering >25% of the panel) and grade 4 means no visible corrosion on the panel surface.

Vapor-phase corrosion inhibiting ability (VIA)[21] tests the products ability to protect metals from corrosion without coming into direct contact. The test is performed as follows: Carbon steel plugs are sanded in one direction with 120 grit silicon-carbide sandpaper and rinsed in methanol. The plugs are then polished at a 90° angle to the initial grind with 320 grit paper, rinsed in methanol and dried. The test apparatus consists of a quart jar with a modified lid (Figure 2). The cleaned plugs are then inserted into the rubber stoppers (Figure 2-B, F). Strips of the test substrate (1" x 6") are hung from the inside of the lid, being sure not to 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. The jars are then placed in a 40°C oven for an additional two hours and after which, they are removed from the oven and the surface of the plugs inspected for corrosion. The plugs are rated on a scale of 0-3 where grade 0 is heavily corroded (showing no corrosion inhibition), while grade 3 means no visible corrosion and good inhibiting effects.

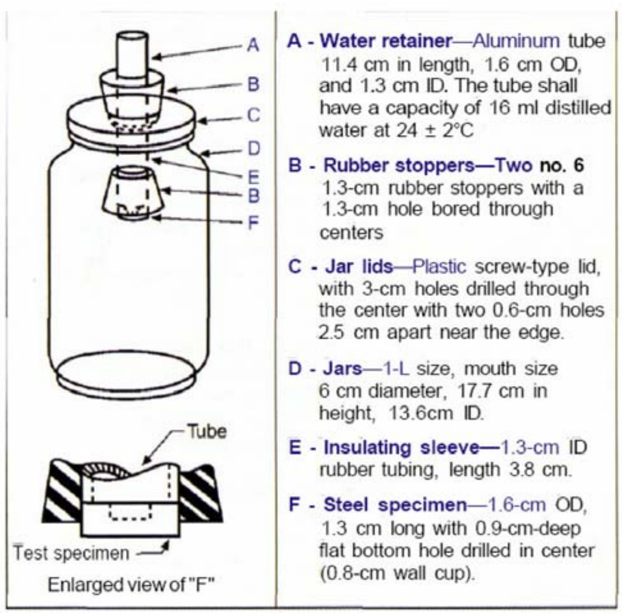

FIGURE 2 - VIA Test Apparatus

RESULTS

The physical properties of the above mentioned products are reported below. For comparison purposes, the grease resistant corrosion inhibiting paper was tested along side polycoated paper and waxed paper, which are often used in grease resistant applications (Table 1). It is easy to see that the grease resistant paper constructed from an environmentally friendly approach demonstrates an equivalent, or higher, level of performance in comparison to traditional products.

TABLE 1
GREASE RESISTANT PROPERTIES

Test Method	Grease Resistant Paper	Waxed Paper	Polycoated Paper
3M Test Kit	9	7	9
TAPPI T-454	1800+ sec	< 60 sec	1800+ sec

The water resistant paper was evaluated for the amount of water absorbed, by a 2 minute Cobb test, as well as for the transmission rate of water vapor (Table 2). The WVTR test was carried out according to ASTM E-96 at 73°F and 50% relative humidity.

TABLE 2
PHYSICAL PROPERTIES OF WATER RESISTANT PAPER

Test Method	Result
Cobb Test	4.0-5.0 g/m^2
WVTR (73°F, 50% R.H.)	3.528 g/day·m^2

The coefficient of friction for the anti-skid linerboard was determined according to ASTM D1894 (Table 3). The test was conducted to determine the COF for linerboard on linerboard as well as linerboard on metal and compared to a commercially available anti-skid linerboard.

TABLE 3
ANTI-SKID LINERBOARD COEFFICIENT OF FRICTION

Test Method (ASTM D 1894)	VpCI Anti-Skid Linerboard	Typical Anti-Skid Linerboard
linerboard to linerboard	0.454	0.295
linerboard to metal	0.243	0.201

The corrosion inhibiting properties of each product discussed are outlined in the tables below. Table 4 describes the contact-phase corrosion protection as determined by the Razor Blade test. Table 5 further demonstrates the contact-phase protection offered by the grease resistant paper for non-ferrous metals such as copper. Table 6 describes the barrier-phase corrosion inhibiting ability of the five products discussed. Lastly, table 7 demonstrates the vapor-phase corrosion inhibition offered by each of these products. The controls employed for each of these tests are a non-coated substrate of the same material, for the grease and water resistant papers the control is virgin base stock (40 and 37 lb/3000 ft^2, respectively), the anti-skid linerboard control is an untreated 42 lb/1000ft^2 linerboard, and the cohesive and masking films utilize an untreated polyethylene film as the control. The test results verify that each of the functional VpCI packaging products described above exhibit excellent corrosion inhibiting abilities in all three phases, contact-, barrier- and vapor-phase.

TABLE 4
RAZOR BLADE TEST RESULTS (CARBON STEEL)

Sample	Panel 1	Panel 2	Panel 3
Grease Resistant Paper	Pass	Pass	Pass
Water Resistant Paper	Pass	Pass	Pass
Anti-skid Linerboard	Pass	Pass	Pass
Masking Film	Pass	Pass	Pass
Cohesive Film	Pass	Pass	Pass
Control	Fail	Fail	Fail

TABLE 5

RAZOR BLADE TEST RESULTS (COPPER)

Sample	Panel 1	Panel 2	Panel 3
Grease Resistant Paper	Pass	Pass	Pass
Control	Fail	Fail	Fail

TABLE 6
SO_2 TEST RESULTS

Sample	Panel 1	Panel 2	Panel 3	Control
Grease Resistant Paper	Grade 4	Grade 4	Grade 4	Grade 0
Water Resistant Paper	Grade 4	Grade 4	Grade 4	Grade 0
Anti-skid Linerboard	Grade 4	Grade 4	Grade 4	Grade 0
Masking Film	Grade 4	Grade 4	Grade 4	Grade 0
Cohesive Film	Grade 4	Grade 4	Grade 4	Grade 0

TABLE 7
VIA TEST RESULTS

Sample	Plug 1	Plug 2	Plug 3	Control
Grease Resistant Paper	Grade 3	Grade 3	Grade 3	Grade 0
Water Resistant Paper	Grade 3	Grade 3	Grade 3	Grade 0
Anti-skid Linerboard	Grade 3	Grade 3	Grade 3	Grade 0
Masking Film	Grade 3	Grade 3	Grade 3	Grade 0
Cohesive Film	Grade 3	Grade 3	Grade 3	Grade 0

CONCLUSIONS

The combination of aqueous, non-toxic coating chemistries has allowed for an expansion in the physical properties achievable for VpCI packaging products. This broadens the application range and markets where VpCI packaging products can be incorporated. As demonstrated herein, this approach has resulted in products varying from grease and water resistant corrosion inhibiting papers to VpCI containing adhesive films and many more possibilities yet to be revealed. The transformation and adaptation towards a “greener” process not only results in environmentally friendly finished products, but it also reduces work place hazards by removing harmful solvents and chemicals from the coating process. Combining green coating solutions to non-petrochemical derived products, such as papers and bio-based plastics, also helps to relieve our dependence on non-renewable energies, while at the same time reduces our carbon footprint and greenhouse gas emissions. Achieving high performance properties of water based and bio-based chemistries has been the most difficult to overcome, but each of the five products discussed have demonstrated the capabilities and potential of green technologies. These properties show that a new approach towards the development of VpCI technologies has begun and indeed a new realm of VpCI packaging products has been achieved and will continue to be expanded upon.

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