

## Surface Modification of Adhesives, Inks and Coatings – The Interfacial Effects

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### **Abstract**

It is well documented that plastics surface modification techniques can greatly improve the acceptance of a wide variety of coatings, adhesives and inks for improved decoration, painting and adhesive assembly. By increasing the hydrophilic characteristics and surface-free energy of plastics, bond strengths can be improved dramatically. It is theorized that interlayer adhesion between decorating and assembly formulations can also be improved by applying atmospheric plasma surface modification techniques. This study examines experimental data which examine the correlations between surface modification and interlayer adhesions of adhesives, inks and coatings.

### **Introduction**

The adhesion strength of inks, coating and adhesives to plastic surfaces which are micro-roughened, polarized, and made hydrophilic by surface treatments such as corona discharge (air plasma), flame plasma and chemical plasma are routinely measured and quantitatively optimized by iterations of peel adhesion testing, lap shear tests, tensile tests, fatigue/tear tests etc. When multiple layers of inks, coatings and adhesives are applied over plastic surfaces and such surface adhesion techniques are applied, it is frequent that these interlayer adhesions are sub-optimized, relying on their formulation chemistries to create satisfactory “wet-to-wet” and “wet-to-dry” adhesions during in-line or off-line processes. For example, applying tape peel adhesion tests following hot air drying of multiple ink layers has lead industry professionals to recognize failed interlayer adhesions most clearly (and intuitively) where the ink colors differ.

Issues pertaining to dry- and wet-trapping of multiple inks during printing processes can become evident in several ways. For example, when dry-trapping in a second pass through printing equipment, solvent ink can sometimes flake off the substrate. This can occur as a result of wax content at the surface of the first layer of ink preventing full adhesion with a second ink layer with similar wax content. There is, therefore, an inherent need to ensure that the second ink is wax-free, so that its surface energy is higher. This issue can also manifest itself in an opposite manner, described as chalking. Chalking occurs when there is insufficient carrier fluid (paste) binding the first ink’s pigment to the substrate. The cause is an incompatibility between the ink and the substrate, even though the ink may be formulated for the specific type of substrate. This is particularly symptomatic of non-porous polymer-based materials such as spunbonded polypropylenes. If the ink vehicles (oils and solvents) quickly drain into the porous polymer structure, it leaves little behind at the surface to bind the pigment to the substrate surface. Therefore, it is prone to be easily scratched off.

Unlike solvent-based inks where binders are dissolved in the ink solvents, water-based inks (and coatings) are formulated with several types of binders which are not soluble in water. These binders are typically composed of a styrene acrylic alkali-soluble binder and a resin emulsion

[1]. The alkali-soluble binder dissolves in alkaline water, which contains ammonium hydroxide. As the ink dries, ammonium hydroxide and volatile amines are gradually removed, but any alkaline material that is part of the binder in the form of a salt will not be volatilized until there is sufficient heat to decompose the salt and liberate the volatile amine. Also, as the ink dries, ammonia and volatile amines leave the ink, and the emulsion particles can “touch” and combine to form a continuous, dry ink film at the plastic surface. Waxes trapped in this continuous ink (coating) film will migrate to the surface and reduce the surface energy. This effect has the advantage of providing good water resistance at the ink (coating) surface, and these lower surface energy components will be attracted to higher energy surfaces.

However, let’s assume that a polyethylene substrate is pretreated by an air plasma discharge and subsequently exhibits excellent adhesion to such a water-based ink. If a water-based coating is applied over the ink and dried, the consequence can be that the water resistance of the coating and ink adhesion were poor. Why? When trapping the water-based ink beneath the water-based coating, the volatile ink components can be trapped if these volatiles are not previously flashed from the ink by heat. As the coating cures and creates a moisture barrier, it encapsulates the volatile amines which exist in the form of salts in the ink. These amines must be driven by heat from the water-based ink in advance of trapping to complete ink-to-substrate bonding, and to allow the coating to form a water-resistant film surface layer.

But what about the interlayer bond strength between a sufficiently dried ink which dry-trapped by another ink color or coating, assuming their formulations are similar? What approaches might optimize this bond? Analysis has been conducted using electro-chemical impedance spectroscopy (EIS) to quantify the interlayer adhesion of coatings. In this area of study, different automotive basecoat/clearcoat systems were tested on their interlayer adhesion with EIS whereby two thin electrode stripes of an electro-conductive ink were applied between two coating layers. Impedance measurements were conducted to find out the effect of moisture on the interlayer adhesion.

The data generated by Miszczyk and Schauer [2] showed a strong sensitivity of the interlayer impedance on the outer air humidity and point out the possibility of following the water accumulation in the interlayer and the formation of the conductive paths. Such phenomena lead to the adhesion loss and delamination between the coating layers. The key finding was that the interlayer adhesion loss followed the same trend as the changes in activation energy, derived from interlayer resistance as measured with EIS. Although some experimental directions can be derived from this work for measuring certain propensities for interlayer adhesion failure, optimization of interlayer ink, coating and adhesive adhesion is yet to be studied. The following experiment was conducted as a first phase toward addressing this question, beginning with an evaluation of interlayer ink adhesion optimization.

### **Methodology / Experimental**

The objective of the experiment was to evaluate the effectiveness of applying an appropriate surface pretreatment technology in promoting and optimizing dry-trap interlayer adhesion involving a solvent-based ink formulation with a highly polar and crystalline polymer. The same evaluation was also desired with a water-based ink and the same polymer. The profile of the experimental is detailed in Table 1 below:

Process Variables	Specification	Additional Specifications
Substrate	Polypropylene	0.5 mil.
Pre-Treat Surface Tension	30 mN/m	Dyne solutions/contact angle
Water-Based Ink	INX Lamiall® Cyan	none
Solvent-Based Ink	INX Lamiall® White	PU-based; Acetate, alcohol
Treatment System	Enercon Plasma	Argon + oxygen
Treatment Density	6W/ft <sup>2</sup> /min	Base and interlayer
Ink Application Method	Pamarco Hand Proofer	165 line engraved roller
Ink Drying Method	Hot Air Dryer	1 min. ; 4 min. room temp.
Test Ink Adhesion Method	ASTM F2252-03	3M Scotch 800 tape; 180°

A flat polypropylene substrate was employed to facilitate a controlled peel adhesion test following substrate printing. The substrate was pretreated using an Enercon atmospheric plasma treating system, as opposed to the use of an air plasma system, to exclude the possibility of treatment variations caused by random filamentary arcs, or by the propagation of migratory fatty acids which may reside within the polypropylene. Key features of atmospheric plasma are its high density, homogenous and uniform discharge that volatilizes low molecular weight surface contaminations, its absence of random surface-arcing filaments, and its surface functionalization capability to promote molecular bonding. The polypropylene substrate was plasma treated to a wide range of surface tensions using an argon/oxygen mixture, initially to establish a threshold of less than 1% peel for both the water-based and solvent-based inks employed. This threshold was found to be at a minimum of 48 mN/m, achieved at a power density of 6W/ft<sup>2</sup>/min. This level of surface tension ensured anchoring of the base ink for second stage interlayer adhesion testing. Inks were applied using a Pamarco hand proofer with 165 line engraved roll at a 45 degree angle to the line of the roller pinch point. The ink was dried for one minute using a hot air gun, then for an additional four minutes at room temperature. Tape peel adhesion testing was conducted according to ASTM F2252-03 using a 180-degree peel technique using a 3M Scotch #800 tape. Following anchorage of the initial layer for each ink, plasma treatment was applied over the anchor ink layer to raise its surface tension a minimum of 8 mN/m over the surface tension of the dry-trapping ink layer to ensure satisfactory wet-out of the second ink layer. It was determined that a power density of 6W/ft<sup>2</sup>/min. achieved this minimum wet-out level of 40mN/m for the solvent ink, and 39mN/m for the water-based ink. Surface tension readings throughout the experimental were initially determined by wetting tension solutions and then corroborated by contact angle measurements.

## Results and Discussion

The trial results are represented by tape peel specimens as displayed in Figures 1 and 2. White solvent ink tape peels were displayed on black backgrounds, and cyan water-based inks were displayed on white backgrounds to provide maximum contrast of ink residues on the clear tape samples.

As can be seen in these Figures, dry-trapping of solvent/solvent and water-base/water-base inks with common formulations and without surface treatment between layers created spotty

interlayer adhesion results. By plasma surface treating base ink layers to a minimum of 8 mN/m above the base dry ink film layer surface tension created greater than 99% interlayer adhesion for these depositions on polypropylene.

### **Conclusion**

These interlayer ink adhesion results seem to indicate that there is an inherent benefit in modifying the base surface of dry-trapped inks. It is possible that plasma treatment provided a micro-etching effect on the ink surface, along with the potential of removing wax films at the base layer surface. The use of oxygen as the reactive component of the plasma gas mixture may also have contributed to the formation of hydroxyl groups and molecular bonds at the interlayer interface. Further research is suggested to explore the potential of using similar protocols to improve interlayer adhesion between coatings, adhesives, paints and other functional and value-adding components for plastics.

### **References**

- (1) Podhanjny, R.M., "Water-based ink adhesion and web temperature", PFFC Magazine, April, 2001.
- Miszczyk, A., Schauer, T., "Electrochemical approach to evaluate