Game-Changing Surface Pre-Treatment Technology

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Abstract
The flexible packaging industry, despite the still-ebbing economy, continues to experience a technological revolution aimed at value-adding graphics, increasing consumer motivation, and delivering sustainable solutions for a host of challenges throughout the manufacturing and distribution chain. High performance package configurations and new printing technologies (notably flexo) continue to drive packaging into existing as well as completely new markets. Statistically, the U.S. flexible packaging industry is expected to experience annual sales revenue growth of 8.1 percent in 2011 according to the Flexible Packaging Association. The Freedonia Group forecasts revenues for the US commercial printing industry will reach $82 billion in 2011 and that US demand for printing inks will grow 1.8% annually to reach $4.8 billion by 2013. And although the global packaging industry is valued at a burgeoning $450 billion, the emerging markets of China and India for example convert only about 7% of all their packaging by the flexographic process. The market growth opportunities for flexographically-printed flexible packaging are therefore vast. As new state-of-the-art package printing technology is installed in these markets and with processing costs under pressure to enable these processes to ramp-up in 2011, surface pre-treatment technologies must become a key enabler relative to higher processing speed, wider widths, and requirements on inks and coatings to transfer and adhere to substrates at these speeds and widths. This paper presents evidence of new flexible packaging print performance opportunities using new atmospheric plasma treatment (APT) technology.

Flexographic Industry Challenges
In its current state, flexography is being challenged economically by market globalization, supplier mergers, and short run digital to name a few. Technically, achieving proper ink transfer and adhesion, reproducible color, and a water/scuff resistant ink film layer on both porous and non-porous substrates are the most daunting challenges. Matching color and ink adhesion performance across printed packaging components and printing facilities are key. Achieving these consistencies on press will continue to require the use of advanced color management tools and techniques, in conjunction with highly uniform surface modification techniques.

Surface Adhesion Challenges
It is understood that conventional solvent-based inks have better substrate wetting characteristics on on-porous materials such as polymer films than water-based inks or UV-based inks, primarily because some of the solvents can “dissolve” the boundary layer to facilitate ink anchorage to a given substrate. Whereas solvent-based inks will usually provide good ink adhesion on some films pre-treated at extrusion, water-based and UV-based inks are less forgiving and require higher substrate treatment levels on most films.

Water-based and energy-curable ink adhesion to films containing high parts-per-million of slip additives has always been a challenge. Earlier formulations of water-based inks used higher levels of VOCs (10% or more) to obtain the necessary substrate wetting and ink adhesion. Today, market and regulatory pressures are pushing the flexo industry to the target of 0% VOCs.

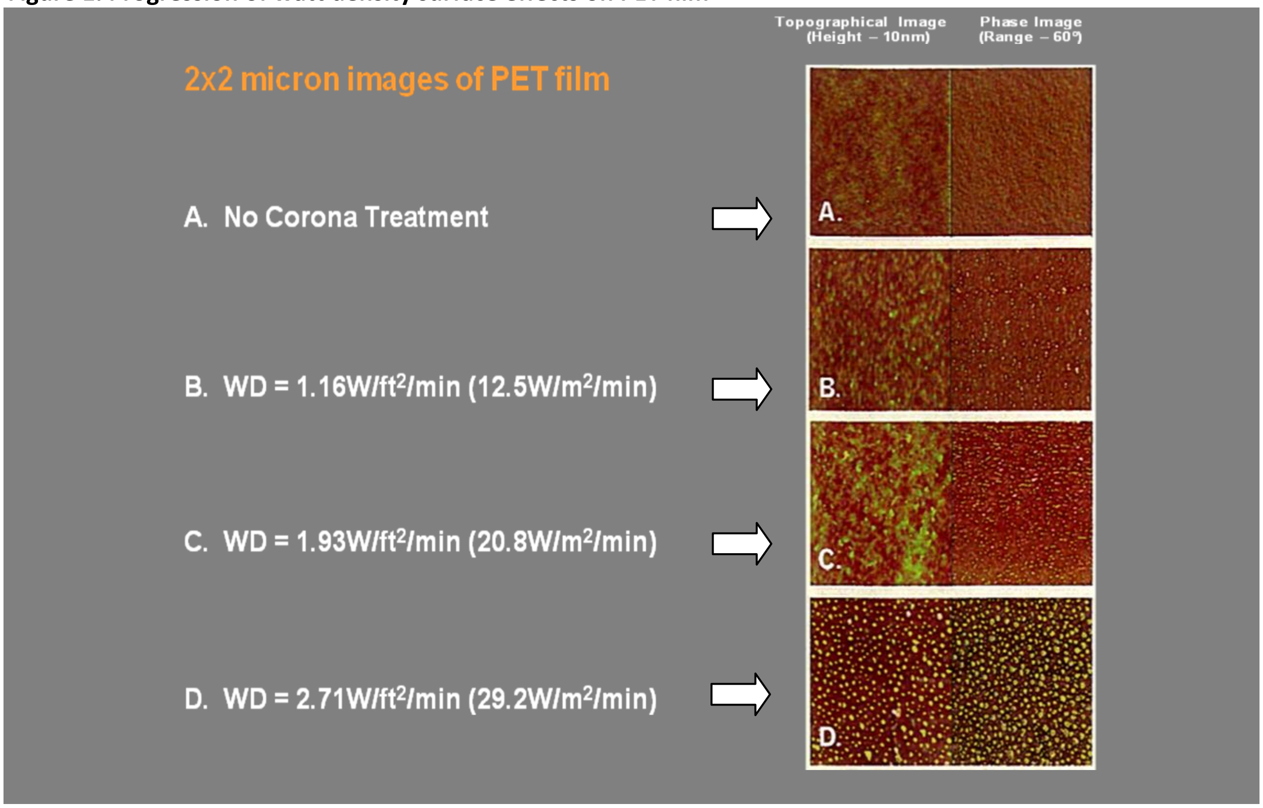
Continued reductions of VOCs in flexo inks requires innovative formulation approaches among ink suppliers to achieve good ink wetting and adhesion to challenging surfaces such as high-slip films. Techniques being used among ink formulators are 1) crosslinking adhesion promoters, 2) high-performance emulsions, and 3) surfactants that can remove the boundary layer. However, the key to achieving high-quality water-based and UV flexographic ink adhesion lies specifically in pigment wetting, ink rheology and the reactivity of the formulated system. Rheological behavior is directly related to pigment wetting and accounts for many of the required performance properties of the formulated ink. These properties provide the formulated ink good dispersion, good flow, good transfer to the printing equipment and to the substrates, correct viscosity, low plate swell, and good print color strength. Other important criteria are surface reactivity, adhesion and odor after drying or curing of the formulated ink.

Successful printing on high-slip films and high surface-contaminated films therefore requires careful analysis of the surface tension characteristics of the film, the required surface treatment process, and the surface tension and formulation of the ink.

Limitations of Current Surface Activation Technologies

Corona treatment has traditionally been used as a surface modification technology with flexography and is helpful to a certain extent, but it is a "variable" treatment. When a polymer film is manufactured, for example, there is always some residual unpolymerized material left in the polymer. This oligomer has a low molecular weight and will easily migrate through the polymer and appear on the surface. The amount of oligomer on the surface will depend on the age and storage conditions of the polymer film roll. If untreated and left on the surface, the flexographic ink will bond to this oligomer which forms a weak boundary layer and will have a poor bond strength to the native film surface.

Figure 1. Progression of watt density surface effects on PET film



Corona treatment will improve this bond, but it first must be optimized in terms of its dielectric configuration and watt density (see Figure 1). And because of the reactive nature of corona treated surfaces to open air, treatment must take place immediately before coatings are applied. Specifically, treatment can vary and degrade with air humidity. Parameters for treatment established on a low humidity day may not be optimized for treatment during humid days. Corona treatment is also not permanent since oligomer present within the bulk of the polymer will re-migrate to the surface following treatment over time, and that rate of migration will vary relative to changes in ambient temperature.

Atmospheric Plasma Technology Change

In recent years, there has been a shift to atmospheric plasma technology (APT) for flexographic applications which require overcoming the limitations of corona treatment. The APT process modifies material surfaces similarly to vacuum plasma treatment processes - the surface energy of treated materials increases substantially, corresponding to enhancements in surface cleanliness, wettability, printability, and adhesion properties. The APT process consists of exposing a surface to a low-temperature, high-density glow discharge (i.e., plasma). The resulting plasma is a partially ionized gas consisting of a mixture of neutral molecules, electrons, ions, excited atomic and free radical species. Excitation of the gas molecules is accomplished by subjecting the gas to an electric field, typically at high frequency. Free electrons gain energy from the imposed high frequency electric field, colliding with neutral gas molecules and transferring energy, dissociating the molecules to form numerous reactive species. Interaction of electrons, UV radiation and excited species with solid surfaces placed in opposition to the plasma results in the chemical and physical modification of the material surface.

The effect of plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma. At the low exposure energies typically used for surface treatment, the plasma surface interactions only change the surface of the material; the effects are confined to a region only several molecular layers deep and do not change the bulk properties of the substrate. The surface is subjected to ablation and activation processes (See Figure 2). Activation is a process where surface functional groups are replaced with different atoms or chemical groups chosen to react within the plasma.

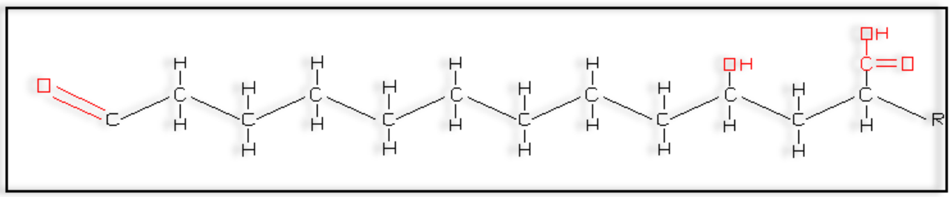


Fig.2 Plasma activation of polymer surface by creation of free radicals through substitution.

The bombardment of surface such as a polymer film with energetic particles and radiation of plasma produces ablation and micro-etching effects. The bombardment by plasma species is able to create a nano-roughness on a polymeric film, for example, that does not modify the mechanical bulk properties of the film but removes low molecular weight surface organics and thereby strongly increases surface adhesion (See Figure 3). Where bond strength is required, atmospheric plasma's highly reactive species significantly increase the creation of polar groups on the surface of materials so that strong covalent bonding between the substrate and its immediate interface (i.e., coatings, adhesives) takes place.

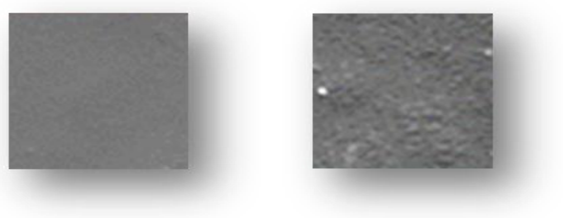
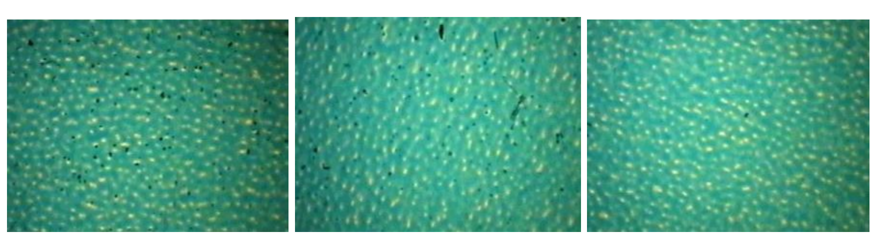


Fig. 3 Atmospheric plasma micro-etching effect of PE film, 30,000 SEM magnification

Surface cleaning via atmospheric plasma techniques reduces organic contamination on the surface in the form of oligomeric residues, anti-oxidants, carbon residues and other organic compounds. Oxygen-based atmospheric plasmas in particular are effective in removing organics whereby mono-atomic oxygen (O+, O-) reacts with organic species resulting in plasma volatilization and removal (See Figure 4).



(a) (b) (c)

Fig. 4 Micrograph of PET film (a) untreated with low molecular weight organic contamination, (b) after corona discharge cleaning, and (c) after oxygen-based atmospheric plasma cleaning.

Atmospheric plasma technology can affectively compensate for many of the shortcomings that corona discharge presents to a flexographic surface adhesion challenge. However, there are application barriers that APT itself its faces relative to its adaptation to large width and high speed production lines. Specifically, APT is a gas-phase discharge which impinges the surface of a moving substrate. High velocity conveyance of substrates will cause a boundary layer of air to attach to the substrate. This air which is forced with the motion of the substrate can cause at least partial separation between the surface of the web and the surfaces of rollers. When this occurs, there is a change in the ability of the plasma discharge treatment process to effectively treat the face side of the web. Diffused and reacted gas chemistries are interrupted from impinging the material surface. As a result, treatment level can decrease as air mixes with the gas. This can also drive-up the voltage required to ionize the changed mixture, as well as create variability in treatment across a moving web. This effect can require increases in gas flow rates to compensate for the boundary layer air effect. The level of significant plasma impingement interruption can vary, dependent upon the surface roughness of the substrate and its speed. A second application barrier for APT pertains to the maximum treatment width achievable using certain ceramic electrode configurations. These electrodes are extruded and cured in kilns. Electrodes extruded in lengths in excess of two meters begin to challenge tolerances for straightness. This issue has limited the production width of APT systems to under three meters in width.

To compensate for these remaining application barriers, new APT technology has sought to 1) eliminate the effect of boundary laver air to remove remaining restrictions on production speeds, 2) reduce increased system gas consumptions caused by boundary layer air, and 3) remove barriers to unlimited treatment widths caused by the straightness limitations resident within the ceramic electrode extrusion process. The following experimental was performed to examine the efficacy of a new design in APT pre-treatment technology.

Experimental Design and Data Analysis

Key metrics for examining a successful bridging to speed and width-independent APT technology include the following:

- Comparative surface energy treatment level and longevity
- Reduction in gas consumption
- Uniformity of treatment

The preliminary matrix for examining these metrics was as detailed in Table 1 below:

Table 1. Matrix of Trial Parameters for 1) standard APT design and 2) large width, high speed APT design change

Material	Initial Dynes/cm	Speed	Carrier Gas	Carrier Gas %	Reactive Gas	Reactive Gas %	$W/ft^2/min$
Pretreated BOPP film	30	300fpm	N2	100	0	0	4.364
Pretreated BOPP film	30	300fpm	N2/H2	90	CO2	5	4.364
Pretreated BOPP film	30	300fpm	N2	100	0	0	2.182
Pretreated BOPP film	30	300fpm	N2/H2	90	CO2	5	2.182

A newly designed 60" wide, open station APT system developed by Enercon Industries was evaluated at high speed with a challenging substrate, a non-polar 2 mil. biaxially-oriented polypropylene (BOPP) film. Trials were run at 300fpm, a speed which is known to force significant boundary layer air with film substrates and to dilute/decrease gas-phase plasma surface reactions. Two gas chemistries were employed in the study – one using 100% nitrogen (higher ionization potential) and a nitrogen/hydrogen/carbon dioxide mix (lower ionization potential) – and two power densities (low and high) for surface energy, longevity, and gas consumption monitoring and comparisons. To further discern the potential for reduced gas consumption by the new technology, the rate of gas introduction was set at 50% less for the new technology.

Results and Summary

Figure 5 below summarizes a comparison of both the current ceramic electrode-based APT and new APT technologies relative to surface tension and longevity of surface tension after treatment at 300fpm and utilizing two different gas chemistries and power densities (PDs). The data clearly indicates that the new APT technology

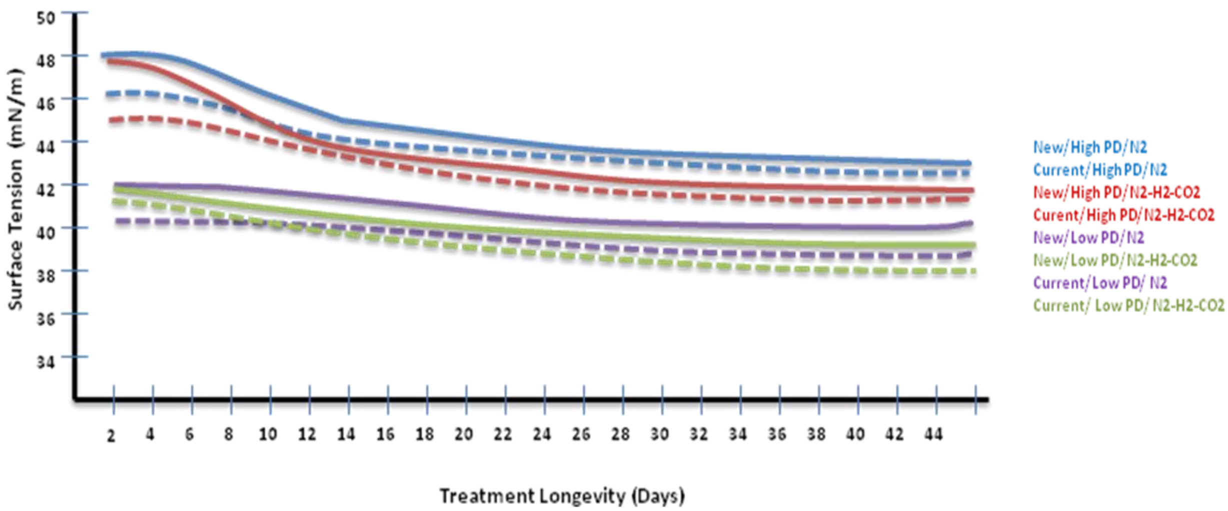


Figure 5. Comparative of new and current APT technologies by surface energy level and longevity of treatment

achieves surface tension levels superior to current ceramic-based electrode APT technology at 300fpm and irrespective of the power density. Concurrent inferences can be made that the current APT system is significantly influenced by the boundary layer air effect, and that this effect is independent of the ionization rate of the different gas mixtures. Furthermore, the 50% reduction is gas consumption with the new APT technology did not have a deleterious effect on treatment level, indicating that this level of reduction in consumption can be practically achieved. Longevity of treatment seems to be comparable to the current APT system design.

Two additional and significant observations made during the experimental was that there was no additional gas flow rate required at a higher test speed of 1400fpm to maintain treat level, and less than 0.1ppm of ozone production was measured at the exit of the new APT system (below OSHA PEL limit), remarkable findings given the system's operation at atmospheric pressure.

It is apparent that new APT technology can offer game-changing surface pretreatment advantages which the flexographic community can leverage to meet competitive global challenges relative to productivity. These systems also offer the potential to deliver 2-3 times the power output of current ceramic electrode APT designs, reducing their in-facility footprint. The results of this study indicate the following step-change in APT capability:

- Higher treatment levels
- No apparent boundary layer air effect on treatment level
- No apparent barrier to operating speed
- No apparent barrier to treatment width
- 50% reduction in operating gas consumption, regardless of speed