Aldyne™ Technology

Atmospheric Pressure Plasma Treatment for Molecular Monolayer Coatings

Summary

Many applications within the converting industry require the use of adhesion promoting primers. Softal and Air Liquide jointly developed Aldyne™, a technology that replaces traditional liquid primers with a cost efficient, and environmentally friendly, atmospheric pressure plasma process. Aldyne™ running costs are typically only 10% of traditional liquid primer processes.

The Aldyne™ process is based on the use of a well defined and controlled gas atmosphere. This provides control over chemical reactions within the plasma as well as on the polymer surface. The results are functional coatings with a thickness of a molecular monolayer, typically 0.3 to 0.4 nm.

Since Aldyne™ does not use any liquid or solid substances, no residues can accumulate. Therefore, costly cleaning procedures are eliminated. Also, within the Aldyne™ treating process, a drying step is not required and the often associated problems regarding removal of organic solvents are not present.

The molecular coatings can be adapted to the converting process. Amido, imido, and amino groups for example provide excellent adhesion to water based, solvent based, and UV drying inks and lacquers as well as adhesives.

Aldyne™ is an inline process and can be easily integrated into existing converting lines and operates at speeds of 300 m/min and more. Major components are a specially designed plasma source that enables control of the plasma gas at the ppm level, a gas delivery system, and a complete and fully automated process control system.

Introduction

Modern flexible packaging for food applications is very often made up of multi-layer structures each one ensuring one or more of the required functionalities of the final material. These are mechanical strength, optical clarity, barrier behaviour towards moisture, oxygen, light, aromas, etc, sealability, printability and slipping to list the most common. Plain or co-extruded OPP, OPET, OPA, PVC and PE films together with aluminium foil, metallised film and/or paper or paper board are used as raw materials and they are converted through surface treatment, primer coating, metallising, printing, lacquering, laminating or extrusion coating.

The quality of a multi-layer structure depends on the strength of the interfaces created between the individual layers. Because the materials used to create these layers often possess different surface properties, i.e. some of them are hydrophobic (e.g. like polyolefins they possess only carbon-carbon and carbon-hydrogen bonds with low surface energy) and some others are hydrophilic (they possess chemical functionalities with increased polarity and therefore high surface energy) they repeal each other and they are not directly useable to be assembled together. In order to overcome this difficulty, one can undertake either surface modification by means of atmospheric plasmas, the most common being performed in air and called "corona treatment" or apply to the substrate a thin coating in the liquid form. The later called primer coating, is chemically multifunctional and after drying or curing has the ability to adhere to both types of surfaces hydrophobic and hydrophilic. More often, both corona treatment and primer coating are needed to perform strong adhesion between two substrates or between a substrate and an ink layer. This combination leads to good technical results but it is expensive given the costs of the chemicals, of drying and of recovering the solvents. In order to overcome these limitations we have developed a new surface preparation process able to replace simultaneously both air corona treatment and liquid primer coating.

Aldyne^{TM} concept

The process is based on our ability to create an oxygen free atmosphere in a limited zone inside an open containment where a two-dimensional substrate is moving at high speed.
When the containment is a hood surrounding electrodes and a backing roller like in an air corona station, then under appropriate gas mixtures and operating conditions, specific atmospheric plasmas are produced conferring to the surface of the travelling substrates extremely thin, molecular reactive coatings able to chemically react with inks, varnishes and adhesives. The concept is depicted in Figure 1 below.

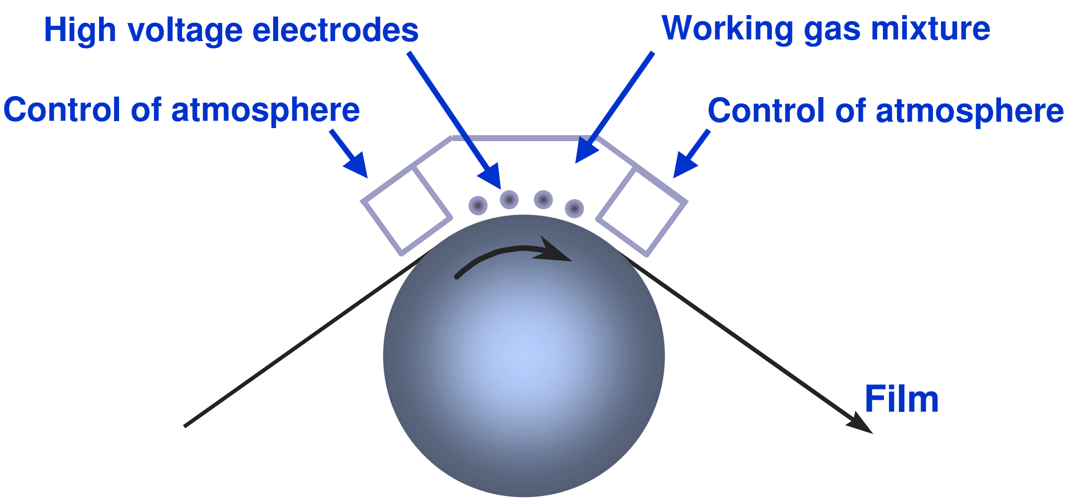
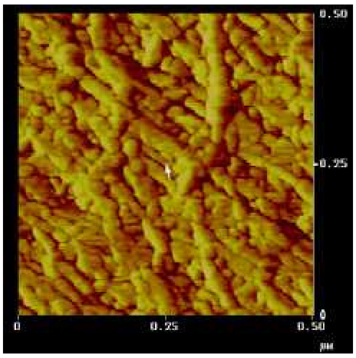


Figure 1: *Aldyne^{TM} concept.*

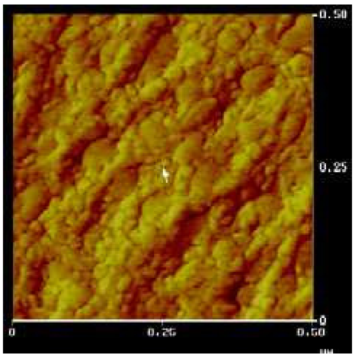
Gas phase primering

Classical air corona treatment is a filamentary barrier discharge in which molecular oxygen is mainly activated producing electrons, meta-stable species, positive and negative oxygen ions, radicals and ozone. All these reactive species occupy the volume inside the "filaments" or streamers arising between the electrodes and have a tremendous effect on organic molecules such as the polymer chains of the film and any oligomer present on its surface (e.g. slip or other type of additive). This effect consists on braking carbon-hydrogen and carbon-carbon bonds, which in turn results in cleaning of the surface (small molecules become even smaller and "burn" or leave the surface as vapours which solidify once in contact with the metallic parts of the equipment) , but also creates erosion or "etching" of the surface of the film by removal of small polymer chain fragments. This chain breaking leads to carbon radicals which react with the excited oxygenated species but also with excess molecular oxygen present in the immediate environment of the carbon radical.

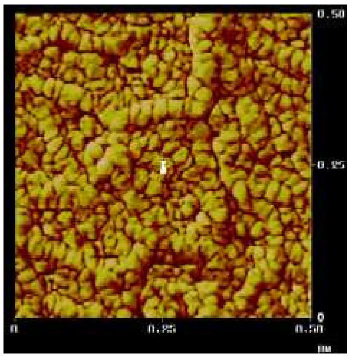
As shown by atomic force microscopy (AFM) pictures in tapping mode of 20 µm thick BOPP film (Figure 2(II) below) after corona treatment the physical morphology of the surface exhibits a much lower roughness than that of the initial substrate with several dark brown zones of higher viscosity having the form of flat elliptical 50nm x 65nm zones and corresponding to the "etched" parts of the material. In terms of chemical modification, x-ray photoelectron spectroscopy (XPS) results summarised on Table 1 show around 14-16% carbon atom substitution by oxygen atoms the later being under the form of carbon-oxygen based functional groups like alcohol, ether, ketone and acid or ester (for analysis of chemical functions see Table 2).



(I) Untreated, Ra = 5.2 nm



(II) Air corona, Ra = 3.6 nm



(III) Aldyne™, Ra = 4.6 nm

Figure 2: *AFM pictures of BOPP (TAPPING mode)*

As a result, one can observe the increase of surface energy due to the grafting of these polar groups and, to some extent, of the adhesion characteristics of the treated surface. However, these surface characteristics are not permanent and surface energy and adhesion decrease fast.

Gas Mixture	Specific Energy (Wmin/m²)	%C	%O	%N	O/C	N/C	N/O
Untreated		100,00	0,00	0,00	0,00	0,00	
Air Corona	50	86,01	13,35	0,64	0,155	0,007	0,048
Air Corona	100	83,93	15,48	0,59	0,184	0,007	0,038
GM1	50	87,42	6,44	6,14	0,074	0,070	0,953
GM1	100	83,93	7,77	8,30	0,093	0,099	1,068
GM2	50	88,69	6,80	4,51	0,077	0,051	0,663
GM2	100	85,68	7,78	6,54	0,091	0,076	0,841
GM3	50	85,30	11,15	3,55	0,131	0,042	0,318
GM3	100	82,54	11,63	5,83	0,141	0,071	0,501

Table 1: *XPS surface analysis of air corona and Aldyne™ treated BOPP*

Like air corona, Aldyne™ takes place in a filamentary barrier discharge. The Aldyne™ plasma is created in nitrogen gas containing small amounts (a few ppm) of added gases such as CO_2, N_2O or H_2. Due to the absents of oxygen, ozone is not produced during the treatment. Compared to air corona, the streamers are shorter, more dense and less energetic because they do not produce etching or other kinds of severe alteration of the surface of the substrate. As shown on Figure 2(III), AFM pictures exhibit only regular weak brown lines on the fibres or lamellas of the BOPP film, with low roughness change, which suggest a much more even and smooth discharge.

As shown in Table 1, the percentage of substituted carbon atoms depends on the gas mixture used and the applied specific energy of the discharge. For three different working gas mixtures (GM1 to GM3) and two different specific energies (50 and 100 Wmin/m²) 12.5 to 17.5% of carbon atoms are replaced by nitrogen (3.5 to 8.3%) and oxygen (11.6 to 6.5%). The gas phase chemistry is then different, and the surface of the polymer is covered by amino, amido and imido groups (see Table 2). From time to time, according to the operating

Gas Mixture	Specific Energy (Wmin/m²)	N1s			
		amine	amide	imide	NR_4^+
GM1	50	36,94	45,38	14,21	3,47
GM1	100	29,06	49,10	19,81	2,03
GM2	50	28,55	50,78	19,62	1,05
GM2	100	29,49	47,08	20,50	2,93
GM3	50	12,13	54,48	32,18	1,21
GM3	100	14,90	49,18	30,80	5,12

Table 2: Chemical functions of Aldyne™ treated BOPP surface

conditions minor amounts of nitrogen in higher oxidation states may be present.
The versatility of the gas combinations, concentrations and flow rates can lead to a variety of amino vs. (amido+imido) groups ratios, namely from 0% amino and 100% (amido+imido) to 50% amino and 50% (amido+imido) functions (not necessarily shown on Table 2). These functions are covalently linked to the surface of the substrate and therefore they are very stable. Also, because the chemically grafted groups are highly polar, surface energies as high as 58 to 60 mN/m are typically obtained for BOPP, as shown on Figure 3.

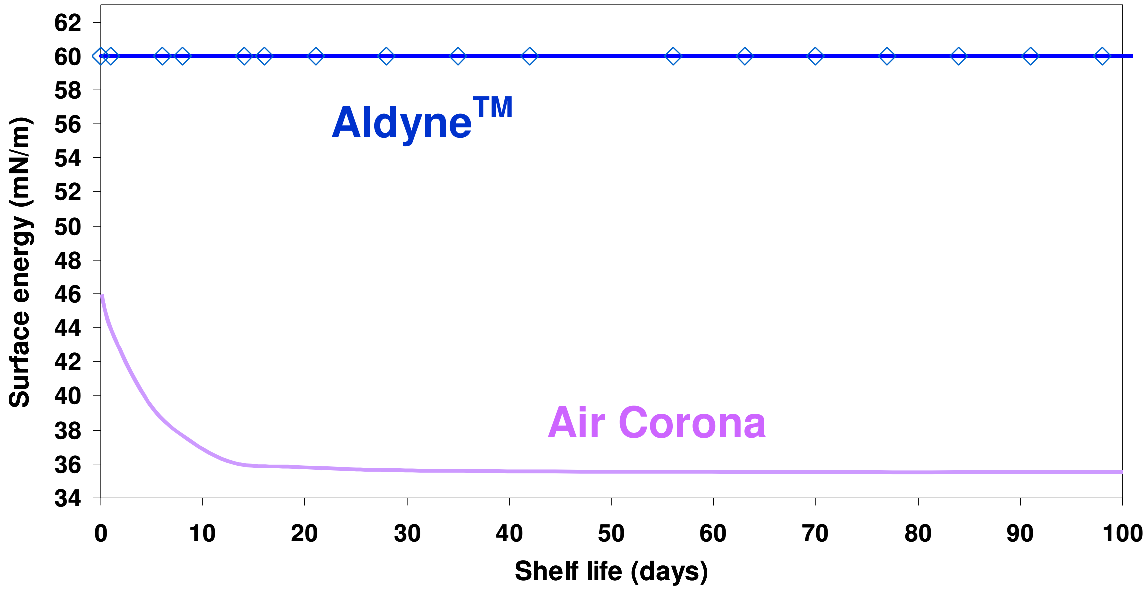


Figure 3: *Surface Energy level and stability of Aldyne™ treated plain BOPP*

The thickness of this gas phase primer coating being very thin (monomolecular layer, a few Å thick) it may be subject to contamination, either external or internal. External contamination can be managed. Internal contamination can result from large amounts of migrating additives (slipping or other kind) and can be detrimental to the shelf-life of the coating, because euricamides, waxes and other similar compounds can mask the surface amino and amido/imido groups. In such cases of large additive content, long storage and transportation of treated materials must be avoided, but in line operations or after short storage converting are feasible.
Amino and amido/imido groups show very interesting chemistry features. In fact, these nitrogen based functions can dramatically improve adhesion via “hydrogen bonding” or “covalent bonding” with various ink formulations containing binders such as alkyds, epoxies , isocyanates or acids and esters (e.g. acrylic acid and acrylates). Particularly:

- amido and imido groups are the most suitable chemical functions to give rise to strong “hydrogen bonding” with carboxylate or carboxylic functions like the ones featured by acrylic acid and acrylates. Aldyne™ gas phase primering will be then fully suitable for printing with either water-based inks or UV curable inks and varnishes, all of them containing binders with acrylate backbones.

- amino groups react very fast with isocyanates to produce water stable urea type covalently bonded structures. Consequently, amino rich surfaces will be preferable for lamination with urethane-based adhesive formulations or printing with urethane modified nitrocellulosic inks.

Globally, Aldyne™ treated surfaces are suitable for:

- Printing and lacquering with solvent based, water born and solventless UV curable inks and lacquers
- Adhesive lamination of two polymers or a polymer and aluminium foil or paper board
- Extrusion coating and extrusion lamination particularly for difficult substrates like BOPP, OPET, OPA
- Metallising

in a very cost effective way, since compared to liquid primer, gas phase primer cost will be lower by a factor of 5 to 10.

To illustrate the above chemical reactivity and subsequent high adhesion, Table 3 summarizes the results from printing of 19 µm plain BOPP with water based Acrylate ink. Ink transfer test using an adhesive tape (reference TESA 4104) was performed at 90° and 180°. Adhesion performance is graduated from 0 to 5. Zero indicates total transfer of ink from the film to the tape while 5 indicates no ink transfer at all. As seen on Table 3, samples treated

Gas Mixture	Specific Energy (W min/m²)	Surface Energy (mN/m)	Tape Test Acrylate ink (blue)	
			90° peeling	180°peeling
AIR	50	42	2/5	0/5
AIR	100	42	1/5	0/5
GM1	50	60	5/5	tearing
GM1	100	60	5/5	tearing
GM2	50	60	5/5	tearing
GM2	100	60	5/5	tearing
GM3	50	60	4+/5	tearing
GM3	100	60	5/5	tearing

Table 3: *Printing results from plain BOPP film with water born inks*

with air corona show very weak adhesion and tape test is graduated between 0/5 and 2/5 (almost all ink is transferred to the tape). On the opposite, tests on Aldyne^{TM} treated samples reach 5/5 graduation for 90° peeling and show tearing of the plastic for 180° peeling, the later indicating that substrate/ink interface is stronger than the plastic itself.

As a conclusion, we can say that:

- Aldyne^{TM} gas phase primering is a high performance low cost technology successfully replacing liquid primer coating on any plastic substrate.
- The process does not use liquid chemistry nor solvents or other VOC , it does not generate off-gases emissions nor produces ozone and it is therefore environmentally friendly.

Turn key installations for web widths up to 4 m and speeds of 300 m/min and more, fully automated, easy to operate and transparent to operators, including gas mixing manifolds and gas supplies are currently offered to converters.

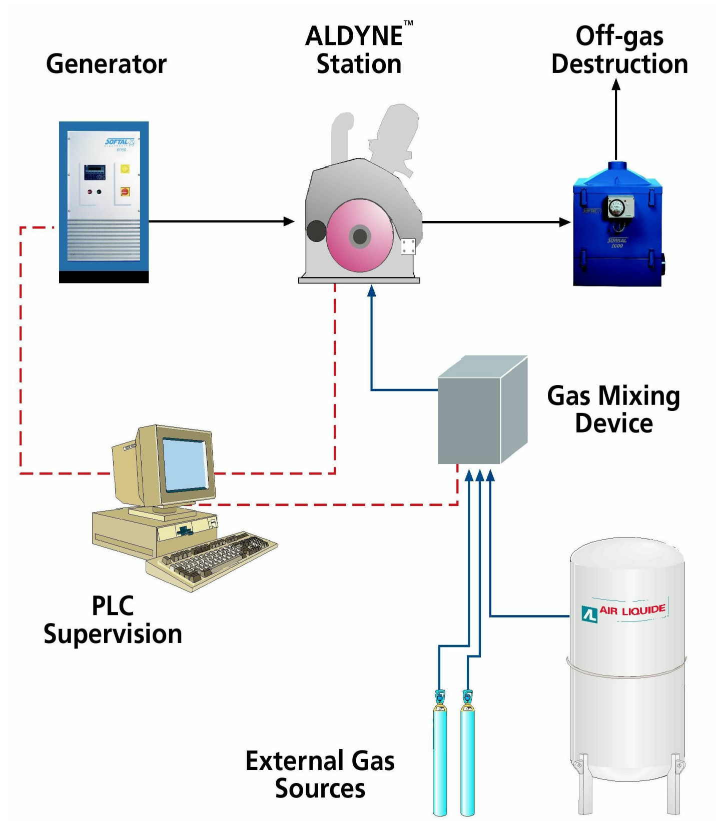


***Figure 4**: Aldyne^{TM} system for molecular monolayer coatings*

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