E 14009 · Volume 17 · September 2011

3·2011

Flexo Gravure Int'l

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The Only Technical Magazine for the Paper, Film and Foil Package Printing and Converting Industries Worldwide

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A G&K TechMedia Publication Made in Germany

Value added oxide coatings for barrier applications

PROFESSOR NADIR AHMED

Clear barrier coated films have become a favoured choice for flexible packaging of various products. At present there are different clear barrier film products available in the market. However, there is always a need for new barrier coatings for existing and future products. This article will discuss the development of a new metal oxide coating to provide a good barrier at a competitive cost. Clear barrier processes can be retrofitted on a standard vacuum web metalliser to provide films with good transparency, high surface wettability as well as gas and moisture barrier. This article will also review the main clear barrier coatings deposited by vacuum technology and will outline the newly developed metal oxide coating as a newcomer to clear barrier films.

Transparent barrier coatings on polymers are receiving much attention for different applications including pharmaceutical, food and beverage packaging. Food packaging is part of our daily life as it protects the integrity of the product. Food can now be stored for weeks or even months on shelves or in refrigerators without losing its freshness or taste.

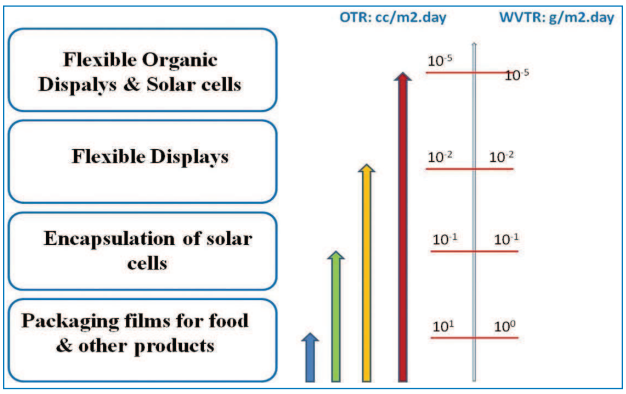
Barriers prevent chemical or physical reactions between packed food products and their environment. This includes dust, contamination, light, mechanical impact, gas, moisture and aromas.

Various packaging materials can provide these necessary barriers to protect and preserve our food, but all have their specific properties and limitations. For example, glass is transparent and is an excellent barrier material, but it is less good against light, it is heavy and breaks under high impact. Aluminium foil is a very good barrier against moisture, gases, contamination, and light, but it provides very little protection against mechanical impact and is very brittle. In cans and glass jars, the moisture and oxygen barriers are provided by the dense nature of the material. With thin plastic films, the situation is different. The molecular structure of polymer plastic films is in the form of chains, oriented like a grid. The more these chains are linked together, the better the barrier will be. The required barrier specifications for different applications are shown in *figure 1*. For food packaging, an oxygen barrier (OTR) of less than 10 would be acceptable for many products.

So far, Aluminium foil was has been considered to be the best packaging material to provide high barrier properties. It is durable to moisture and gases regardless of its thickness. However, Aluminium foil at thicknesses of less than 25 microns has pinholes which have an impact on the barrier properties. The foil also has its limitations particularly in terms of cost and transparency. As the price of raw materials increases and the requirement for see-through products, particularly in food packaging, becomes more demanding, Aluminium foil starts to give up to other types of packaging products including Aluminium metallisation and clear barrier coatings.

Figure 1 (below):* *Barrier specifications for different products.

Figure 2 (right):* *Dry food packaging with transparent window.



Barrier selection criteria

The selection of a barrier for a particular product depends on many factors. These can be summarised as follows:

1. Type of material required to provide oxygen, water vapour, aroma, chemical, UV light, and/or microbial barrier properties. This will suppress oxidation of protein, fats, and oils as well retaining freshness and taste.
2. The compatibility of a barrier material with the packaging material and product. For example, if the product chemically reacts with the barrier material.
3. The barrier material should not be affected by converting equipment used to process the packaging material.
4. The barrier material should not be affected by the sterilisation method, environmental conditions and or disposal method.
5. The barrier material should not add too much to the final cost of the packaging.

To meet most of these requirements, metallised Aluminium films have been used since early 1970's in packaging applications for decorative, food, biomedical and electronic products as an alternative to Aluminium foil. The quality of the metallised coatings is usually measured using several parameters which include surface finish, optical density, surface resistivity, gas and water vapour barrier.

Reasons for clear barrier coatings

There are increasing demands by consumers for see-through food packaging with a high degree of transparency, long shelf life and the

ability to cook by microwave technology. Aluminium foil or metallised films are unable to provide such

Managing Director *Idvac*, Manchester/GB. www.idvac.co.uk

a combination of properties, whereas polymer-based barriers coatings are well suited.

The degree of transparency of a polymer layer will depend on its structure (amorphous, i.e. transparent, or crystalline, i.e. translucent) and its thickness. In some cases, e.g. for replacing cans by retorting in flexible pouches for shelf-stable products, the barrier should ideally be both heat-resistant and transparent. For many applications, there are conflicting interests between product visibility and light protection. To some extent, the problems can be alleviated by using small see-through windows rather than fully transparent packages (*figure 2*). As the demand for clear packaging and fast microwaveable food has increased, transparent thin film barrier materials based on oxides of silicon and Aluminium and melamine have been developed. Such materials can provide a similar performance to metallised films but with high transparency.

Advantages of clear barrier coatings

There are many advantages to using clear barrier coatings for food packaging. These can be summar-ised as follows:

1. High degree of transparency which allows microwaveability, retortability, metal detection during and after manufacturing of the finished packaging, visible inspection and long shelf life.

2. Some oxides such as silicon oxide and Aluminium oxide are more environmentally friendly compared to conventional Aluminium foil or polymeric clear coatings such as EVOH, PVdC or PVC.

Currently, most transparent flexible barrier films are produced using polymeric barrier layers including EVOH and PVdC. The thickness of such layers is in the range of several micrometres to several tenths of micrometres. However, some of these coatings contain chemicals such as chlorine, which are not considered to be environmentally friendly.

Usually, films with polymer resin compositions such as PVA, EVOH, PVdC and PVC are laminated to provide clear barrier films.

However, some polymer resins such as PVA or EVOH have high-temperature and humidity dependency which lowers the gas barrier property. Therefore, boiling or retort treatment during converting affects the barrier properties of the laminated film.

The alternative technology for thick polymeric coatings such as PVdC or PVC can be a vacuum coating process with a coating thickness several orders of magnitude thinner and in the range of only ~10 nanometres. This can achieve the same or better barrier properties compared with polymeric coatings. Another advantage of vacuum based processes is that the source materials for the barrier layers are usually natural occurring oxides like SiO_x or AlO_x.

Although environmental aspects, barrier and optical properties are all important, equally important are the cost aspects, process flexibility regarding different base films and coating robustness to survive the converting processes. *Table 1* shows the clear barrier requirements for different food products.

Applications and the world production of clear barrier films

Most applications for clear barrier coatings are for fresh and processed food packaging. *Figure 3* shows the application of clear barrier films for different products. Dairy products are in third position.

Figure 4 shows the world production of SiO_x and AlO_x clear barrier coatings for packaging. In 2009, Japan exported between 80–100 million sqm (861–1076 million sqft) of transparent barrier films, mainly SiO_x and AlO_x to Europe. According to the research association *Pira International*, the global demand for clear barrier coatings is forecast to grow by 4.3% per year by 2014. Other forecasts indicate a figure of 5–10% annual growth. In Great Britain the main applications of SiO_x and AlO_x barrier films are in meat packaging.

Vacuum coating techniques used for clear barrier products

There are three main vacuum web coating processes used for the production of clear barrier coatings: Sputtering, electron beam and thermal resistance evaporation.

Sputtering is based on the utilisation of energetic ions produced by dense plasma on a magnetron sputtering target. The ions bombard the target at a high energy level causing the target material to be ejected and deposited on the film (substrate). Sputtering provides dense coatings and is used for many technical applications which demand high quality specifications. However, the sputtering process usually runs at relatively low coating speeds resulting in higher coating costs. Also, sputtering web metallisers are expensive compared

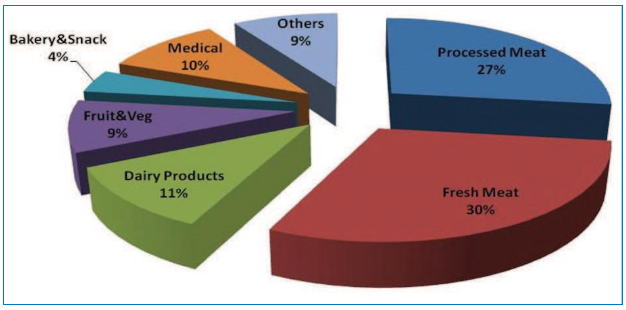


Figure 3 (above): Applications of clear barrier films in packaging. Source: Flexible & Plastic Packaging Innovation, Vol.2, Issue2, 2008.

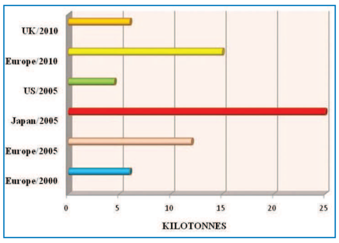
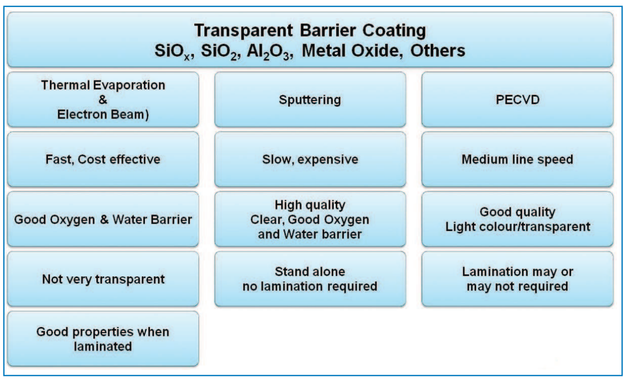


Figure 4 (left): World production of SiO_x and AlO_x clear barrier films (in 1000 mt/a).

Product	Primary	Secondary	Tertiary
Fresh meat	Oxygen	Moisture	Light, aroma
Dairy products	Oxygen, light	Moisture	—
Condiments	Oxygen	Flavour	Moisture
Coffee	Oxygen	Moisture, light	—
Potato chips	Moisture	Light	Oxygen
Bakery goods	Moisture	Flavour	—

Table 1: Clear barrier requirements for food products.

Figure 5: Vacuum techniques used for the production of clear barrier.



to standard thermal evaporation web metallisers.

Electron beam evaporation uses an electron beam to evaporate the material from a water-cooled crucible. With this process different types of materials can be evaporated. However, electron beam vacuum web metallisers are expensive and require highly skilled operators to run the process. The third and most common process is standard web metallisers which use thermal resistive evaporation. This type of machine uses standard resistively heated boats and can be converted for other value added coatings. Standard web metallisers are less expensive than hightech sputtering or EB metallisers.

In recent years, new technologies have been introduced for conventional thermal evaporation web metallisers to improve coating quality. This includes the introduction of plasma treatment and plasma reactive (assisted) evaporation for clear barrier product such as Aluminium oxide. *Figure 5* shows different types of vacuum coating techniques used for the production of clear barrier films. Chemical Vapour Deposition (PECVD) is based on the injection of silicon gas into gas plasma to deposit SiO_x on the film.

Vacuum coating materials for clear barrier

Aluminium oxide (AlO_x)

It can be produced by different coating methods. In a sputtering machine, Aluminium or an Aluminium oxide target is sputtered in the presence of oxygen plasma. In an electron beam evaporation machine, Aluminium or Aluminium oxide is reactively evaporated from a crucible in the presence of oxygen plasma. In standard thermal evaporation Aluminium metallisers, the machine can be converted to the AlO_x process by evaporating a thin layer of Aluminium in the presence of oxygen or ions. A controlled injection of oxygen is directed towards the Aluminium vapour stream causing a reaction between the two elements to produce AlO_x. This compound can be transparent if the process conditions are correct. AlO_x clear barrier films based on this process are already available in the market. With a closed loop process control, a good water and oxygen barrier is achieved without the need for exotic and expensive vacuum ancillaries, such as plasma guns. This process is based on the utilisation of an advanced control loop which constantly monitors the optical properties of the coated substrate to control the injection of the oxygen into the system. Although AlO_x coated films are used for food packaging applications, it has limitations for some food products since it may react with the contents resulting in the loss of barrier property. However, the AlO_x process uses a very low level of process consumables, enabling low-cost production of a relatively high priced coating to be achieved.

Silicon oxide (SiO_x)

Silicon oxide coatings are applied using different vacuum web coating techniques. It can be applied by sputtering, electron beam evaporation or by modifying the resistive heating source in a standard Aluminium metalliser. In EB and thermal evaporation processes, solid silicon oxide is heated to its sublimation temperature in a vacuum.

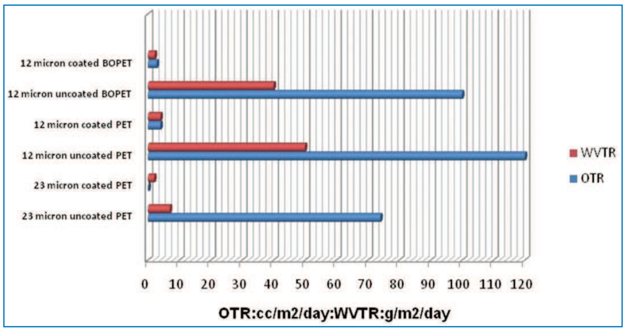


Figure 6: Comparison between barrier properties of metal oxide, SiO_x and AlO_x on 12 and 23 micron PET film.

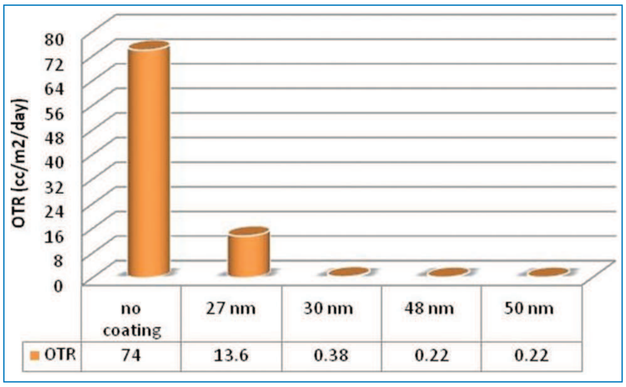


Figure 7: The effect of metal oxide coating thickness on 23 micron PET film.

The SiO_x vapour then condenses on the substrate, forming a very thin barrier layer on the film. The thickness of SiO_x thin layer is between 40 and 80 nanometres depending on the application.

Chemical vapour deposition (CVD) is also used to deposit a clear SiO_x coating on film. This process involves plasma decomposition of 1,1,3,3-tetramethyldisiloxane (TMDSO) or hexamethyldisiloxane (HMDSO) using a 40kHz oxygen and helium plasma discharge onto polymeric webs. The films are coated at 50 mTorr process gas pressure. Common polymer packaging films such as PET and OPP are used as substrates. However, the cost of

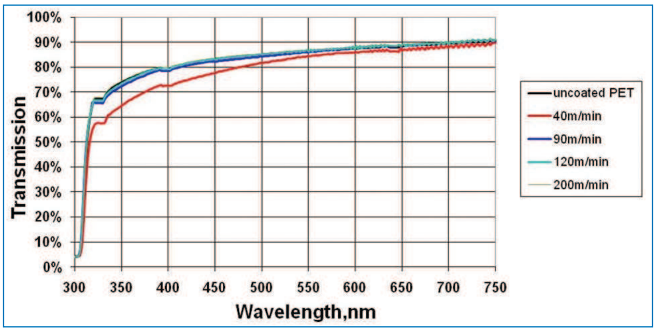


Figure 8: Optical transmission and atomic force microscopy picture of metal oxide surface.

such process and equipment is high. In general, SiO_x coatings provide excellent oxygen and water vapour barrier properties. The main drawbacks with SiO_x are the limited flex and crack resistance and the relatively high production costs. The mechanical resistance can be improved by covering the SiO_x layer with a varnish, or by lamination of the SiO_x coated substrate. However, SiO_x performs favourably when compared to Aluminium foil and metallic composites. SiO_x coating is available in grades appropriate for retort/autoclave applications. Due to the initial cost of the material, SiO_x coated films are more expensive than standard metallised Aluminium and AlO_x clear barrier coatings. Because of the many advantages of clear barrier coatings including transparency and microwaveability, the extra cost of SiO_x is often justified.

Freshure process

Recently, *Knowfort Technologies BV* (*DSM*) has developed another process for clear barrier films. This involves the application of additional organic topcoat such as melamine on the inorganic AlO_x layer for the barrier application. This process is called *Freshure*.

Development of a new clear barrier coating

Recently, *Idvac* has developed another type of metal oxide barrier coating. This coating can be applied on polymeric films such as PET inside a standard vacuum web metallisation machine. The inorganic metal oxide can be evaporated in a vacuum environment at a lower temperature than SiO_x. This means that the process can run at faster line speeds. The thickness of the coating is between 45 and 80 nanometres according to the application. Barrier tests are usually conducted on clear barrier film to check the barrier performance. Oxygen and water vapour transmission rates are measured using equipment with modern controls according to *ASTM* standard methods. For oxygen transmission rate (OTR), *ASTM D-3985* is used at 23 °C (73 °F) and 0% RH. For water vapour transmission rate (WVTR) *ASTM F-1249* standard is used at 40 °C (104 °F), 90% RH. Some equipment has a couple of test cells running simultaneously for statistical accuracy. *Figure 6* shows the barrier properties of *Idvac* metal oxide compared to others such as SiO_x and AlO_x.

The effect of coating thickness on a barrier for metal oxide on 23 micron PET film is shown in Figure 6. It is evident from *figure 7* that OTR is reduced when the coating thickness exceeds 35 nanometres.

Characterisation of the Idvac metal oxide coating

The characterisation of the metal oxide coating can be summarised as follows:

– Refractive index: 1.7;
– Highly-conformal – uniform coating;
– Low stress – good adhesion;
– Amorphous/semi crystalline surface structure (*figure 8*);
– Good transparency (figure 8);
– Lower evaporation temperature than SiO_x, .i.e. does not require EB evaporation. This means less heat load on the film.
– The coating is antistatic.

Water contact angle of metal oxide coating on PET

The water contact angle of any clear barrier film is preferably not less than 30° when defining the moisture vapour barrier property after an inorganic thin coating layer has been vapour deposited. *Figure 9* shows the water contact test of the metal oxide deposited on PET film. It is evident from this picture that the angle is about 70°, which means that the coating/PET surface has good surface energy and barrier properties (*table 2*).

Lamination of clear barrier films

Clear barrier vacuum coated films are usually laminated with materials for retort or non-retort applications. The laminated substrate enhances the moisture and oxygen barrier of the structure (*figure 10*). Lamination also protects the coating from mechanical damage during the converting process.

A heat-sealable resin layer is formed by the dry lamination method. A thermoplastic polymer forming a heat-sealable resin layer may be used as long as the sealant adhesiveness can be sufficiently expressed. Polyethylene resins such as PE, LDPE, LLDPE, PP resin, ethylene–vinyl acetate copolymer and ionomere resins can be used.

Water contact angle (°)	Surface energy (mJm^{-2})	Polar contribution (mJm^{-2})	Dispersive contribution (mJm^{-2})
76 ± 1	35.7	7.37	28.3

Table 2: Metal oxide coating water contact angle and surface energy.

Retrofits of clear barrier coatings onto standard web metallisers

Retrofitting a standard vacuum web metalliser for other value added coatings in addition to standard Aluminium represents a cheaper option for the following reasons:

1. Introduces a new business opportunity to meet the market demand for new functional coatings.
2. Offers flexibility for a wide product range.
3. Offers a technical lead ahead of the competition.
4. Introduces new technology to a standard machine.
5. Offers the opportunity to explore new markets and applications.

However, a retrofit is usually kept to a minimum and does not interfere with the flexibility of the machine to produce standard Aluminium metallised products. This makes a standard Aluminium web metalliser more flexible in meeting some of the demands for new value added products and emerging markets, particularly when the selling price of metallised Aluminium per kilogramme becomes very competitive. *Idvac* has developed a range of retrofits to convert standard Aluminium metallisers to enable the production of new value added coatings/products (*figure 11*).

Summary

In comparison with wet polymeric atmospheric coating, vacuum coating only requires a small fraction of the thickness of the equivalent atmospheric coated layer to produce similar functionality. Typically, atmospheric coatings are measured in micrometres (10^{-6} m) while, vacuum coated layers are measured in nanometres (10^{-9} m). The barrier properties of the two structures are similar. This creates a huge environmental and economic advantage for vacuum coating technology.

Most clear barrier coatings available in the market are natural oxides and are not toxic or dangerous to the environment or individuals. Recycling and waste management is relatively cheap and simple. In combination with a compostable substrate, it can even be fully biodegradable.

The vacuum production process is usually based on well accepted and reliable advanced systems. The standard vacuum web metalliser layout provides optimum flexibility, depending on the actual needs of the customer. Metallising of different types of transparent barrier processes can be accomplished by standard or specialised web metallisers. Selecting the most convenient clear barrier coating depends on the application. Currently, there is a wide variety of clear barrier materials from which to choose. However, clear barrier films produced by vacuum technology are the favoured choice for many demanding products. ■

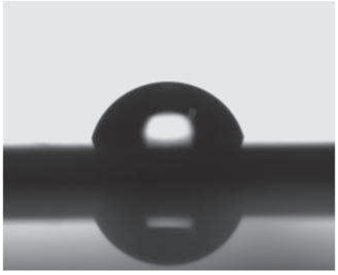


Figure 9: Water contact angle testing of metal oxide coating.

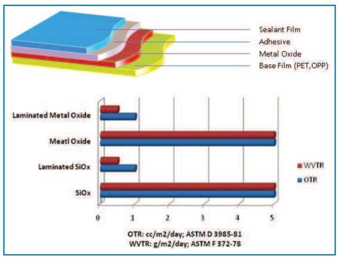


Figure 10: Standard lamination of a clear barrier coating on 12 micron PET film for protection.

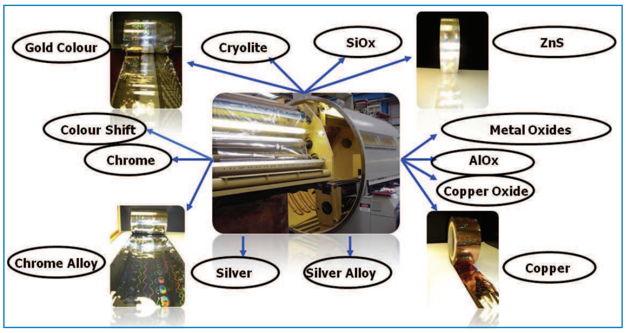
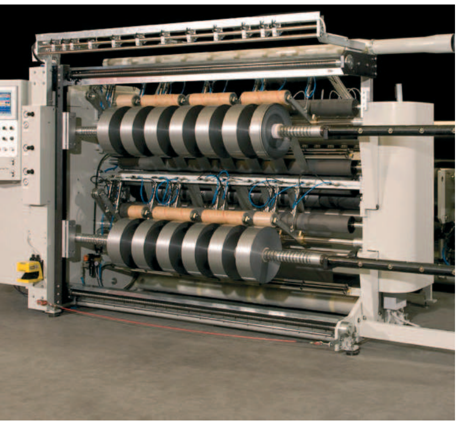


Figure 11: A range of value added coatings produced by a standard Aluminium web metalliser.

Big sister

BIELLONI ■ The *B87* series of slitting machines has been extended to include a new model with a working width of 2000 mm (78.7"). The ma-



chine offers a production speed of over 300 m/min (984 fpm) and all functions are programmable by means of a *Siemens* computer with a touchscreen. The computer stores all machine job parameters and tensions and provides alarms for eventual faults and operator errors.

The machine is equipped with a shaftless unwinder for reel diameters up to 1200 mm (47.2"), Slit reels may have a maximum diameter of 600 mm (23.6"). Small slitting widths of 50 mm (1.97") can be achieved.

The slit reels are automatically ejected by an electric unload system. The machine is additionally equipped with a hydraulic rotating device for easy unloading of the slit reels. This machine is particularly interesting for all operations which initially produce wide mother reels (CPP, hard PVC, OPP, soft PVC, PET, PA, etc.)

➜ *www.bielloni.it*

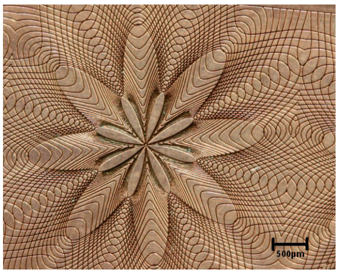
New dimensions

FLINT GROUP ■ The *rotec Atlas Airo Adapter* range has been expanded. In order to offer the complete portfolio of adapters in the premium segment, the adapter is now available in wall thicknesses from 15.9 mm to 100 mm (0.63"–3.94") for specific printing presses. The adapter shows its excellence, especially at high press speeds due to its vibration-damping carbon fibre structure. Results have shown that the *rotec Atlas Airo Adapter* can cover a huge variety of different printing jobs with excellent print performance. Because of the smaller wall thickness and the special construction, printers can now benefit from the outstanding performance of the adapter, even for smaller repeats and cope with the highest printing requirements.

➜ *www.flintgrp.com*

Residue-free direct laser engraving

HELL GRAVURE SYSTEMS ■ Seven years after the introduction of *Cellaxy*, the pioneer in direct lasering of Copper gravure cylinders presents



Cellaxy LightPeak, a direct laser engraving technology which opens up a whole host of new applications above and beyond conventional Copper gravure. *LightPeak* enables *Cellaxy* to perform high-quality direct lasering for embossing technology, printed electronics, and highend security printing.

In addition to Copper, other materials can be processed such as Steel, Zinc, Nickel, and Aluminium. New, attractive areas of application are made possible for *Cellaxy*, particularly in combinations of applications and materials. Initial productivity comparisons show that direct laser engraving with *LightPeak* far outstrips established technologies on the market. A further benefit of residue-free laser engraving using *LightPeak* is that there is no need for an additional finishing process such as electropolishing. *LightPeak* is an innovative laser modulation technology which brings together the benefits of CW (continuous wave) and pulse lasering.

When combined with a screening technology specially developed by *Hell*, *LightPeak* achieves outstanding results in direct laser engraving in terms of both quality and performance.

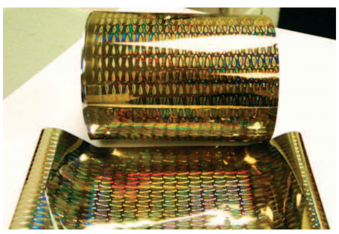
➜ *www.hell-gravure-systems.com*

Yellow Gold vacuum metallisation process

IDVAC ■ The vacuum coating solution supplier has developed a vacuum metallisation process to convert standard Silvery coloured metallised films into Yellow Gold colour without using any wet chemical dyes. In this process, standard Aluminium metallised films which are Silvery in colour are converted in a vacuum into Yellow Gold colour with different shades. Golden colour can be applied on topside, backside or both sides of standard Aluminium metallised films or papers.

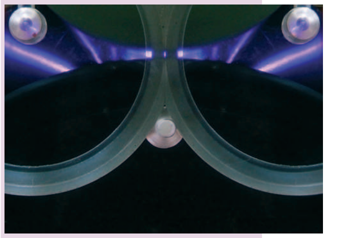
The present processes to achieve a Golden colour on standard metallised films use wet chemical dyes, which turn into a Golden colour once it is coated with Aluminium, or when Aluminium is lacquered by the chemical dyes. The application of chemical dyes onto films or papers requires the use of wet coating machines and chemicals. This new process is dry, vacuum-based, environmentally friendly and cuts the cost of using wet chemical dyes. The vacuum colouration of standard metallised substrates is carried out inside a standard vacuum web metalliser at an average line speed of 200–300 m/min (656–984 fpm) depending on the Gold colour shade required. Metallised films such as OPP, BOPP and PET and metallised paper can be Golden coloured in this process.

➜ *www.idvac.co.uk*



Where economy and ecology merge

ENERCON ■ *Plasma4 is a new atmospheric plasma surface treatment technology that delivers new levels of surface treatment performance with ecology and*



economy in mind. This technology provides striking features such as an efficient design for the most economical use of gas; elimination of electrode breakage; prevention of ozone generation; a large operating window to reduce scrap material; the generation of high and long lasting treatment levels; and an automatic gap adjustment for thickness variations in material. Moreover, the technology offers a wide operating range from low to high speed. Plasma4 is ideal for processing substrates like engineered films and nonwovens.

➜ *www.plasma4.net*
➜ *www.enerconind.com*

Superior characteristics

SIEGWERK ■ *The Sicura Flex 39-10 LM series fulfils the specific migration limits for food packaging in all conventional applications. The inks exhibit excellent flowability, good adhesive properties, and low viscosities. Their high reactivity enables high machine speeds, representing a significant gain over the existing LM flexoprint series. Since the new inks are silicone-free, they can be used without problems for thermal transfer printing; hot embossing is another possibility.*

➜ *www.siegwerk.com*