A simpler package deal

Gel-based multicolour flexo printing system allows single-stage EB curing

by Rob Schellekens

The good physical properties of radiation-cured inks may reduce the cost and weight of packaging by eliminating laminating processes. However, there are concerns over photoinitiator toxicity. Gel-based inks have been developed for electron beam curing (without photoinitiator). Because the inks gellify immediately upon lay down, ink flow and the need to cure individual colours by UV is eliminated.

The print market, in particular converted flexible packaging, faces increasing pressure to reduce the environmental impact of packaging. The packaging structure itself, along with the production and printing process, are all under continuous study to reduce their carbon footprint.
A primary path used to achieve this objective is the reduction of weight by using lighter gauge substrates, and increasing interest in reducing or even eliminating multiple layer structures and/or lamination steps [1].
In the printing process itself, the reduction in use of organic solvents to reduce VOC emissions has become a key objective. The solvent in conventional inks functions predominantly as the "carrier" for the solid portion of the material. In most cases, solvent emissions are handled by thermal oxidation (incineration) which produces greenhouse gas (CO_2).
Solvents are highly refined materials derived from fossil hydrocarbon sources. It is quite wasteful to use such a high-value material for such a low-value temporary function [2]. Solventbased materials are an old technology that is clearly out of step with a sustainable future.

Limitations of waterbased ink technology

Waterbased inks would appear to be an attractive choice from an environmental perspective and they occupy an expanding position in the field of printing. Water is a relatively plentiful, low-cost and environmentally friendly carrier.
The main disadvantage with water however, is the large amount of energy required to remove it from the solid portion of the formula. This high energy requirement is easily illustrated by comparing some heats of vaporisation:
» Water = 540 calories/gram
» Propylene glycol = 62 cal/g
» Toluene = 88 cal/g

The generation of energy needed to operate the driers to remove water results in significant CO_2 emissions. In addition, most waterbased materials do contain some solvents to aid the formation of the polymer film upon drying the ink, coating or adhesive.
Also, solvent- and waterbased materials are usually applied at 30-40 % solids, whereas energy cured materials are normally applied at 100 % solids. A significant reduction in transport costs and greenhouse gases is associated with using energy cured inks, as they reduce the volume to be transported to about one-third.
In addition, waterbased inks and coatings do not always have the resistance or appearance properties to match higher performance solvent- or UV/EB-based materials.

Limitations of radiation curing in flexography

Electron beam energy curable inks enjoy a growing interest by brand owners, printers and converters, especially for food packaging applications [3]. Its sustained success in offset printing, which has its focus on paper and paperboard printing, has made EB curing the technology of choice in that market space. However, there has been strong growth in flexible packaging, which is predominantly printed by flexography and primarily by "central impression" (CI) flexography, as the compact machine design allows extensible substrates such as polyethylene to be printed. Environmental pressures, cost reduction and improved print quality have all pushed ink manufacturers towards UV curing in this printing segment too. Print quality and environmental concerns have been resolved; however market penetration has been limited due to:
» Migration concerns;
» Odour issues with photoinitiators;
» The high power of inter-station UV curing of individual ink colours can damage thermally unstable films;
» Cost of UV inks;
» High power costs.
To address the limitations of UV curing for the CI flexo market, the concept of eliminating the intermediate curing stages has been researched and introduced by some manufacturers. This requires the viscosity of the first inks applied to be increased by temperature differences [4] between the inks or by evaporation of a solvent such as water.
This viscosity increase is essential to allow the layers to be laid down without losing the definition of one colour relative to another (referred to as "wet trapping") [5]. However, the technical success of wet-on-wet trapping is hard to sustain consistently and challenges remain for long runs, fine screen printing at high resolutions and commercial speeds.
A new technology to address the market need of EB curable CI flexo inks is described below. This facilitates uncured trapping by the formation of an organogel that is then cured by EB at the end of the printing process [6]. This EB curable CI flexo ink technology is called "Gelflex-EB"; it was developed and launched in 2009 in Brazil.

The nature of electron beam radiation

EB radiation is a form of ionising energy that is characterised by its relatively low penetration and high dose rates, allowing the commercial production speeds required for packaging applications without the use of photoinitiators.

Figure 1: Ink trapping under 150 X magnification: left, offset FM screen with 20 µm dots; right, flexo "Gelflex-EB" inks at 70 lines/cm

As a product or material passes under the beam, energy from the electrons is absorbed that creates free radicals directly on the functional groups present in the ink or coating This absorbed energy alters chemical bonds within the polymers of the ink.
The curing of polymers by electron beam changes a thermoplastic material into a thermoset. When polymers are crosslinked, the molecular weight increases and any movement is severely impeded, making the polymer more resistant to heat and solvents. This locking together of molecules is the origin of all the benefits of crosslinking, including improvement of the following properties:
» Thermal: resistance to temperature, ageing, low temperature impact, etc.
» Mechanical: tensile strength, modulus, abrasion resistance, pressure rating, creep resistance, etc.
» Chemical: solvent and stress crack resistance, etc.
These high resistance properties allow for surface printing and in a growing number of cases the option to avoid lamination steps, reducing the total weight of the package.

How high-performance EB inks reduce package costs

A good example of substantial gauge reduction combined with excellent surface resistance is in the market for outdoor bags, which are heavy gauge PE and frequently laminated. The lamination is intended to protect the printed image.
An EB printed PE bag without lamination has all the required characteristics, including controlled coefficient of friction to allow stacking of the bags, UV light resistance and excellent mechanical, chemical and thermal strength. The bag is more

Results at a glance

››› Despite environmental concerns, solventbased inks are still widely used. Waterbased inks may have high energy demands for drying and inferior physical properties.

››› Conversely, radiation-cured inks can have very high levels of physical properties, sometimes allowing cost and weight reductions in packaging by eliminating lamination.

››› However, there are concerns over the hazards of photoinitiators, and in flexo printing (widely used for packaging) the low viscosity inks usually require curing of each individual colour to avoid "ink trapping" problems.

››› A solution has been developed in the form of gel-based inks designed to be cured by electron beam (requiring no photoinitiators). The inks are fluid enough for flexo printing at moderately raised temperatures but thicken rapidly on cooling, providing effective ink trapping in the wet state.

Figure 3: Heating the gel ink from 25 °C (left) to 45 °C (right) dramatically reduces its viscosity

economical to produce, with a lower carbon footprint, yet still maintains all its required functional aspects.

Other successful examples in today's flexible packaging market of the elimination of laminated structures are cut-size A4 wrapping paper (replacing reverse printed laminated duplex paper-PET structures by single layer PET) and BOPP polypropylene confectionery and candy bags and wrappers as well as ice-cream wrappers.

How organogel inks achieve wet trapping

Printed flexible packaging is a market that will continue to grow for some time yet [7]. EB inks benefit in terms of a dramatic reduction of the use of solvent. However, the printing process in EB inks requires final drying, and thus must allow trapping of the inks without drying between consecutive layers.

As flexographic inks – unlike pasty offset inks (*Figure 1*) – are low in viscosity, this has proved to be an assignment with substantial hurdles. Water-based wet trapping inks have been introduced, but the diluent character of water requires too much attention for ease of industrial use.

Technosolutions has developed an EB curable ink, where the trapping is based on laying down a liquefied ink on a viscoelastic organogel. Simply put: wet-on-gel trapping. Organogels are non-crystalline, thermally-reversible solid materials composed of a liquid organic phase entrapped in a structuring network (see *Figure 1*). The liquid can be, for example, an organic solvent, a mineral oil or a vegetable oil.

The solubility and particle dimensions of the structuring agent are important characteristics for the elastic properties and firmness of the organogel. Often, these systems are based on self-assembly of the structuring molecules. Organogels are used in pharmaceuticals, cosmetics, art conservation and food, and now attract interest for use in inks or coatings. The new organogel inks are based on the mechanism of Hansen Solubility Parameters (HSP) [8].

The use of a gel is powerful and effective alternative way to obtain colour trapping of layers of uncured ink. Wet trapping of liquefied inks can only be controlled by viscosity, and this viscosity is easily affected by temperature or by the addition of small amounts of diluents. In an organogel-based system, a solvent is not necessary for dilution as such, but only to adjust the solubility parameters of the medium, thereby liquefying the gel to make it compatible in the medium.

5 % to 10 % of solvent is required to adjust the solubility parameter and allow the gel to be dissolved in this reactive medium. As energy curable inks have a volumetric lay-down of about three times less than solventbased inks, the solvent reduction compared with these solvent based inks is up to 90 %, and one full-blown flexo press may be able to run 24/7 with low solvent emissions and so without the need for solvent incineration.

The significance of solubility parameters

The HSP system has been developed as a way to predict when one material will dissolve in another and thus can form a solution. The basic idea is that 'like dissolves like' where one molecule is defined as being 'like' another if it bonds to itself in a similar way.

Each molecule is given three Hansen parameters, measured in $MPa^{0.5}$:

δ_d The energy from dispersion forces between molecules;

δ_p The energy from dipolar intermolecular forces between molecules;

δ_h The energy from hydrogen bonds between molecules.

Hansen Solubility Parameters have been used in the paints and coatings industry to understand and control solvent/polymer interactions. Although HSP have been criticised in the past, the simple predictive theory of HSP is often used with reasonable accuracy for formulation.

The gel is formed by the use of a gelling agent added to the formulation. PVB (polyvinyl butyral) having partial solubility in the reactive medium is used as a gelling agent. The medium contains oligomers such as epoxidised soybean oil acrylate to influence the speed of the gelling process. The reactive monomers are generally TMPEOTA (trimethylolpropane ethoxy triacrylate), TRPGDA (tripropylene glycol diacrylate), TMPTA (trimethylolpropane triacrylate) or mixtures of these materials.

The use of the PVB is in general restricted to less than 5 % of the total formulation, being less than 2.5 % for most colours. The ink is thermo-regulated having a viscosity of less than 1000 mPa.s.

As the solvent used to adjust the solubility parameter is the monomethyl ether of propylene glycol with an evaporation rate of 62 (butyl acetate = 100), there is only a little evaporation of solvent during the process, decreasing the addition of solvent per hour of operation from 22 l in the case of solvent-based inks to a maximum of 2.5 l/h in the case of an EB gel ink.

Figure 3 illustrates the same varnish (10 % PVB in TMPEOTA) at a room temperature of 25 °C in the gel state (*left*) and liquefied after heating at 45 °C with a viscosity of 357 mPa.s (*right*).

Press requirements summarised

The gel technology has been developed for use in current commercially available press technology. Although new ink formulations are under further development for future press designs, the "Gelflex-EB" inks can be used in any existing CI flexo press with closed doctor blade chambers.

The press would require thermoregulation of the ink, as well as online acoustic viscosity meters or similar instruments. The intrinsic viscosity of the ink in its fluidised state in the ink system on the press is not always unambiguous. Mechanical instruments such as falling-ball type viscosity meters are therefore unsuitable.

The pumping system must be capable of working with higher viscosity fluids, preferably up to 1500 mPa.s. But other than

these requirements, a (retrofitted) EB unit is all it takes to print in an EB ink system.
EB curing for curing printinks will have to take place under inertization, to avoid that oxygen (O_2) will react under the beam of electrons, forming ozon. The commonly used medium is nitrogen (N_2) with a high level of purity (>99.99 %). Such inertization is an integral part of an EB unit, and the radiation chamber thereof. N_2 is most commonly supplied from an outside pressured tank and has on average about 100 m^3 per hour N_2 consumption. As an indication, N_2 has a cost of less than EUR 0,15 per Nm^3 in Europe and the USA.

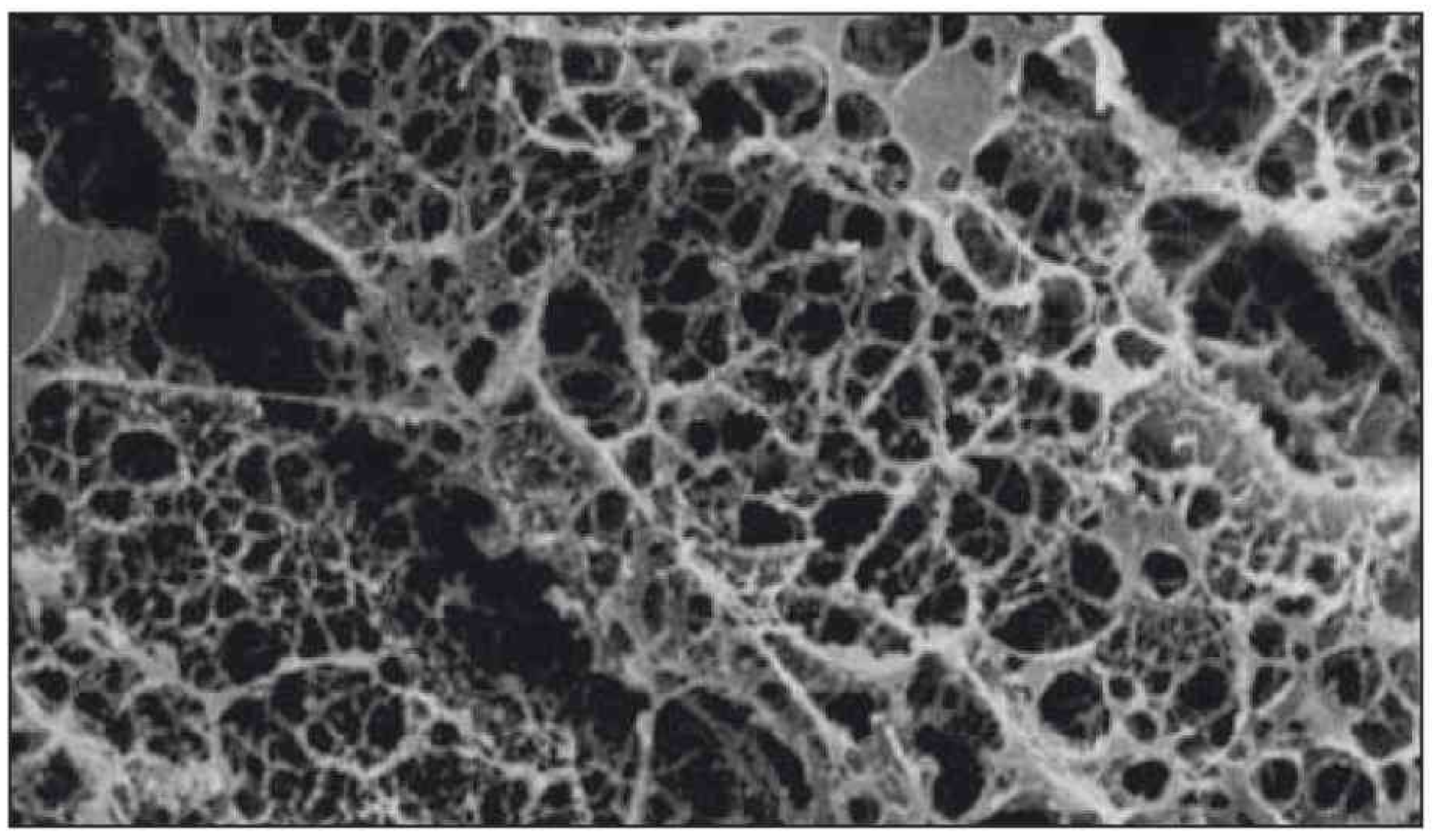

Figure 2: Organogel seen under 10,000 X magnification

Market perspectives

As in any market, the marketplace for printing inks for the converted flexible packaging market is under continuous development and adaptation to shifting market needs. However, the traditional technologies for printing and its applications are mature and not subject to substantial technology migrations.
Consequently, innovations in ink technology have not successfully surfaced in the market. However, whereas printing companies define differentiated strategic goals such as increasing profitability, implementing lean principles, reducing carbon footprint and process improvement, ink manufacturers predominantly retain their traditional product portfolio.
Solventbased inks today remain the products most widely used world-wide, despite the extensive use of hydrocarbons and its impact on carbon footprint. Not without reason, brand owners and retailers are increasing pressure on their upstream supply chain to reduce VOCs, while governments introduce new directives to encourage emission reduction on greenhouse gases.
Gravure is traditionally a dominant technology in Asia, whereas Europe has a mixture of flexo and gravure, and the Americas are dominated by flexography. A few years back, offset technology with its good capabilities in energy curable printing, appeared to claim a place in the packaging market, but this momentum seems to have passed by, as the print quality of offset no longer offers a significant quality differentiation.

Market trends favour flexography

The main factors for choosing a print technology are no longer based on print quality issues. Today's flexographic printing plates give screen resolutions with a print quality similar to gravure and offset. Where the renowned Heidelberg sheetfed printing quality was considered "Art Print Work", today's flexo presses produce comparable results in print quality with ease.
Moreover, traditional printing with flexo and gravure presses are not affected by the high financial investments associated with an offset machine, nor do they have the chemical issues associated with dampening solution in the ink-water balance when offset printing films and foils.
Recent market projections indicate that flexographic inks will remain the leading type of ink used on flexible packaging, supported by the growing popularity of flexible packaging, which utilises flexographic printing as its process of choice. Flexography accounts for almost two-thirds (about 63 %) of the printing technology used in flexible packaging.
Smaller and increasingly sophisticated job runs will also favour flexography, based on recent improvements in both quality and consistency, which have enabled it to compete successfully with the gravure and lithographic printing process. The trend lines and today's market demands for the industry have been clear for many years.
Cost-awareness and profitability is accompanied by increasing demand for short runs, more stock-keeping units, colour consistency, all requiring investment in staff training. Markets in Asia, India and Brazil have moved ahead of North America and Western Europe as the largest flexible packaging market, using the latest innovative technologies.
Interest in sustainability is running high, but concerns over the costs associated in going green are often expressed. Current areas under development include:

» Reducing the volume of packaging waste.
» Replacement of glass bottles, aluminium and tinplate cans and cardboard packages by flexible alternatives, often with better recyclability.
» Use of thinner substrates.
» Reduction of number of layers used, e.g. using energy curable coatings in place of lamination.

Plastic packaging offers a growing market for inks

According to a recent report from Pike research [9], eco-friendly (sustainable) packaging will nearly double its revenues between 2009 and 2014, where it is anticipated that plastic packaging will be the fastest-growing segment of the sustainable packaging sector.
A related question is: what is the ink producing sector adding to support this? Waterbased inks enjoy increased interest, but concerns remain over their performance quality, they still emit VOCs, but also CO_2 emissions are substantial as the use of high powered heated air dryers is required.
Energy curable inks have excellent functional performance, but the photoinitiators in UV curable inks are perceived as a problem.
The ideal technology for many packaging application is therefore electron beam curing, which so far still remains a rather under-used field of operation.
EB curing is an excellent ink technology, which requires end drying. However, wet trapping ink systems in flexo have proven to be a 'hard nut to crack'. The new gel inks offer a route to a new era.
The system is commercially available and has been operational in Brazil since 2009. One of the end-users is Antilhas LTDA in Sao Paulo, Brazil, winner of a prize awarded in 2011 with a cosmetic shopping bag for L'Oreal printed by EB flexo with " Gelflex–EB ". The first installation in Europe is under construction and is due to start up at the end of 2012.

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