Self-curing acrylate resin for UV consumer product printing and coating applications

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Allnex

INTRODUCTION

The discovery of contamination with Isopropyl Thioxanthone (ITX) in various Nestlé baby food brands in 2005 caused a huge stir in the European food packaging market. Millions of liters of product had to be withdrawn from store shelves. At that time, ITX was used as a photoinitiator in UV curable printing inks on the outer surface of liquid milk cartons. Despite the presence of aluminium as a functional barrier, ITX was transferred to the inner side of the packaging through set-off in the reel. In contact with the food, ITX migrated from the inner side of the packaging into the food.

In 2009, the German authorities reported a migration of 4-Methyl Benzophenone (4-MBP) from cardboard boxes produced in the Netherlands containing muesli above the Specific Migration Limit (SML). In this case, 4-MBP, present in an over print varnish (OPV) migrated through the cardboard and its polyethylene liner (which is not a functional barrier either), into the muesli. In this case, the muesli manufacturer (after consultation with the food authorities) decided to take remaining muesli inventories off the market.

Both ITX and 4-MBP issues have put the use of UV curing for food packaging in a negative spotlight. Both standard photoinitiators were able to migrate into the food due to their very small molecular weight (about 200-250 Dalton). Since then, to improve the safety of UV curable inks and varnishes, so called polymeric photoinitiators have been developed. With polymeric photoinitiators, reacting the functionalized photoinitiator to a polymeric backbone increases its molecular weight and by doing so decreases its potential to migrate. The molecular weights of polymeric photoinitiators are typically 700 Dalton or higher.

Examples of polymeric photoinitiators are shown below:

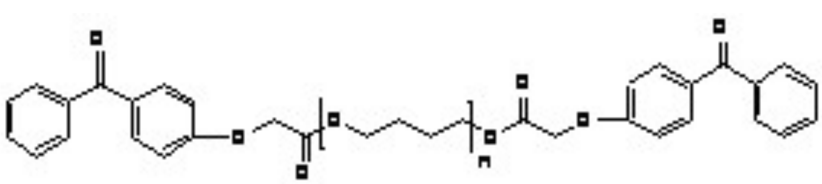

Fig.1: “polymeric benzophenone”

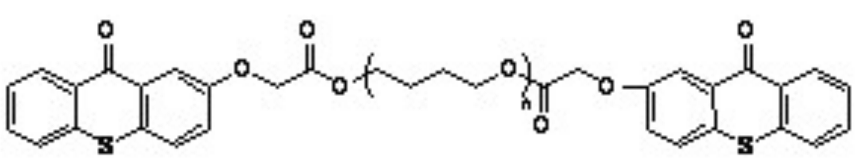

Fig.2: “polymeric ITX”

Polymeric photoinitiators can suffer some draw backs such as:

- Poor solubility in acrylates
- Reduced ink flow leading to problems in ink transfer in ink ducts and ink rollers
- Low reactivity making it necessary to reduce printing speed

To overcome above issues, Allnex has developed a “self-curing acrylate resin” which makes the addition of photoinitiators in printing inks or varnishes unnecessary.

SELF-CURING ACRYLATE RESIN CRITERIA

In the development of our self-curing acrylate resin, the following criteria were applied:

1. Molecular weight of about 1000 Dalton which is the limit above which a product is of “no toxicological concern”
2. Very high purity to avoid low molecular weight impurities and / or residuals prone to migration
3. The ability to generate free radicals upon UV irradiation
4. No generation of low molecular weight breakdown products
5. Build into the acrylate matrix formed during curing of inks or varnishes

For point one, the goal is finding the right compromise between increased molecular weight on the one side, but keeping the viscosity low enough and the reactivity high enough.

To reach the required purity levels necessary for indirect food packaging, a selection of high pure raw materials and an optimized process were required.

Points four and five were “solved” by the development of a new photoinitiating species not cleaving under UV irradiation, built in the product matrix.

In order to reach the desired reactivity and to avoid resin migration, the resin contains acrylate functionalities which fix the self-curing acrylate resin into the matrix of the cured film, thus drastically reducing the risk of migration.

APPLICATION PROPERTIES OF SELF-CURING ACRYLATE RESIN

What are the application challenges faced by self-curing acrylate resins?

Reactivity in printing inks systems must be high enough to be able to print at speeds of 250 m/min and higher. Furthermore, the printing ink must have the desired reactivity for a wide range of pigments. Often, photoinitiator packages are optimized for the different pigments as pigments with a different chemical substrate absorb UV light at different wavelengths, making part of the UV light unavailable for initiating the polymerization reaction.

Secondly, the self-curing acrylate base resin needs to be versatile enough so that it can be used in different application techniques such as flexo, offset etc…In flexo high reactivity at lower viscosities is required. Good ink water balance in offset printing ensuring good press performance…

As a part of this project, an extensive assessment of the application properties of the self-curing acrylate resin in different application technologies such as Over Print Varnish (OPV), flexography and offset were performed. Application performance results are described below where a 30% amount (by total formula weight) of self-curing acrylate resin has been formulated into black and white flexo inks and then into magenta offset inks.

Application results in BLACK FLEXO ink

Table 1 below provides a formulation example using 30% self-curing acrylate resin resulting in an ink with a viscosity of 1000 mPa.s at 25 °C. This energy cured ink was evaluated against commercial and lab made inks using standard photoinitiators (3% phenyl benzophenone (PBZ), 5% Ethyl-4-dimethyl aminobenzoate (EDB) and 1% Irgacure 369 from BASF) and polymeric photoinitiators (“optimized” PI blends in the lab; 10-12% in total in the ink) respectively.

Component	**%**
EBECRYL® LEO oligomer	11.0
EBECRYL® LEO diluting acrylate	13.7
Dispersing Agent	2.2
Stabilizer	0.1
Pigment Black 7	18.0
Grinding on triple roll mill	
Self-curing acrylate resin	30.0
EBECRYL® LEO diluting acrylate	25.0
Mixing and viscosity adjustment	
	100.0

Table 1: Formulated black flexo ink using EBECRYL® LEO products (LEO = Low Extractables low Odor).

Reactivity (Fig. 3) was measured with a 120 W/cm mercury lamp on a 1.2 g/m^2 thick ink film by talc. When no talc stain remains, the ink is considered dry. The results are given as total energy dose required (mJ/cm^2). The need for a higher dose to full cure indicates a lower reactive system and vice versa. The results clearly show the high reactivity level obtained with the self-curing acrylate resin in a black flexo ink. Darker colored inks are considered to be the most difficult pigmented inks in regards to curing in energy cured flexography.

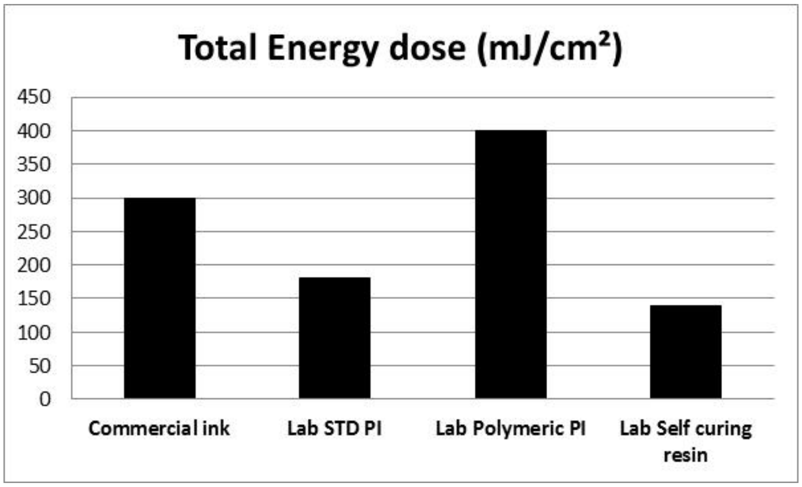

Fig.3: Reactivity of black flexo inks: total energy dose in mJ/cm² to obtain a dry film (1.2 g/m²).

One of the draw backs of the polymeric photoinitiators mentioned earlier in this paper is their reduction of ink flow. It is particularly important for flexo inks to have a good flow in the ink chamber and whilst they fill and empty the anilox cells. It is also important to have a quick air release from the ink.

Flexographic ink rheology is measured with a plate and cone rheometer indicating how close a flexo ink is to a Newtonian behavior which is ideal for flexo printing. A simple measurement of ink flow by a flow plate also gives a good indication of Newtonian behavior. Results of the four different ink systems are given below in Fig. 4. The ink based on self-curing acrylate resin chemistry compares well with commercial inks and lab standard inks, whereas the ink using polymeric photoinitiators clearly lacks flow.

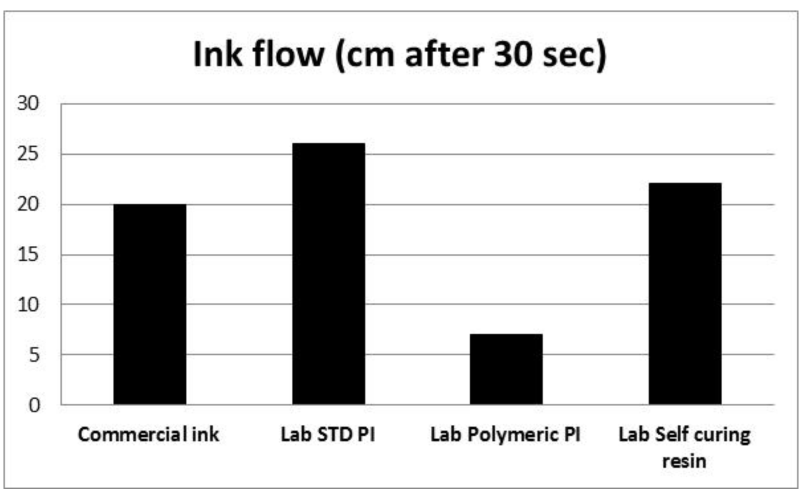

Fig.4: Ink flow in cm of black flexo inks, using 3 g of ink and 30° flow plate angle.

Application results in WHITE FLEXO ink

In flexo packaging printing, about 40% of all ink consumption is white e.g. when printing in reverse (first colours followed by a white solid covering the full surface). Obtaining good reactivity in white inks is challenging as titanium dioxide based pigments (TiO_2) absorb a big part of the emitted UV light from a Mercury lamp. Traditionally, for titanium dioxide based white pigments phosphine oxide photoinitiators are used.

In Table 2 below an example is given for a formulation using 30% self-curing acrylate resin resulting in an ink with a viscosity of 1000 mPa.s at 25 °C. This ink was evaluated against commercial inks and lab made inks using standard photoinitiators like 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TPO) and Bis Acyl Phosphine Oxide (BAPO).

Component	**%**
EBECRYL LEO® Polyether tetra Acrylate	23.9
EBECRYL LEO® TMP(EO)$_4$TA	5.0
Dispersing Agent	1.0
Stabilizer	0.1
Pigment White TiO_2	40.0
High speed dispersing	
Self-curing acrylate resin	30.0
Mixing	
	100.0

Table 2: Formulation for white flexo ink using EBECRYL LEO® products.

Reactivity (Fig. 6) was measured with a 120 W/cm mercury lamp on a 2 g/m² thick ink film by graphite. When no graphite stain remains, the ink is considered dry. The results are given as total energy dose required (mJ/cm²). The need for a higher dose to full cure indicates a lower reactive system and vice versa. The results are exceptional. The dose needed to cure the white flexo ink using the self-curing resin is much lower.

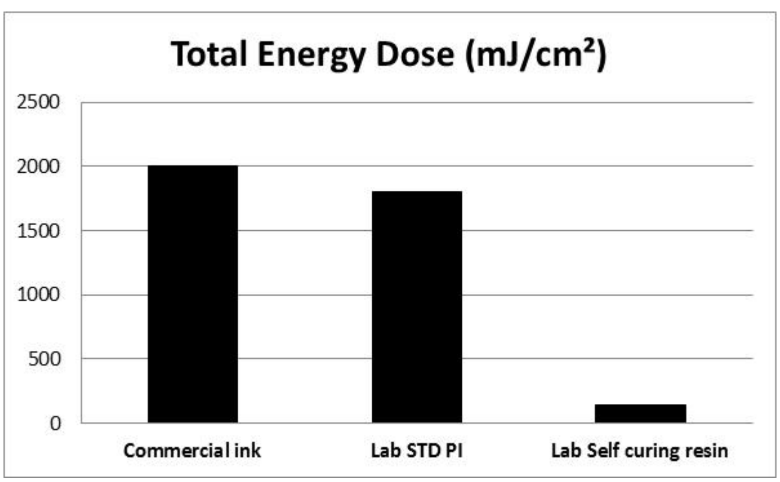

Fig.6: Reactivity of white flexo inks: Total energy dose in mJ/cm² to obtain a dry film.

Fig.7 shows that no yellowing occurred during and after curing thus resulting in a nice white ink.

Fig. 7: Comparison of whiteness/yellowing: commercial white flexo ink (left) versus self-curing acrylate resin based white flexo ink (right) at 2 g/m².

Application results in MAGENTA OFFSET ink

Offset printing is known for its high print quality, high dot definition with high print contrast. In paper and board packaging Offset has been used for decades and is making inroads into flexible packaging via VSOP (Variable Sleeve Offset Printing) presses.

In Table 3, an example is given of a magenta offset ink formulation for paper & board using 30% self-curing acrylate resin resulting in an ink with a viscosity of about 40 Pa.s at 25 °C. This ink was evaluated against commercial inks and lab made inks using standard photoinitiators (a eutectic blend of benzophenone, ITX, Ethyl-4-dimethyl aminobenzoate (EDB) benzyl dimethyl ketal (BDK)), (Irgacure 369-BASF) and polymeric photoinitiators ("optimized" PI blends in the lab); 15% in total in the ink) respectively.

Component	**%**
EBECRYL® LEO Polyester acrylate	22.0
EBECRYL® LEO Epoxy acrylate	24.0
EBECRYL® LEO TMP(EO)$_4$TA	5.0
Stabilizer	0.1
Talc	3.0
Pigment Red 57:1	18.0
Grinding on triple roll mill	
Self-curing acrylate resin	30.0
Mixing	
	102.1

Table 3: Formulation for magenta offset ink using EBECRYL LEO® products.

Reactivity (Fig. 8) was measured with a 120 W/cm mercury lamp on a 1.2 g/m² thick ink film by graphite. When no graphite stain remains, the ink is considered dry. The results are given as total energy dose required (mJ/cm²). The need for a higher dose to full cure indicates a lower reactive system and vice versa. The results indicate a similar reactivity level is reached using the self-curing acrylate resin.

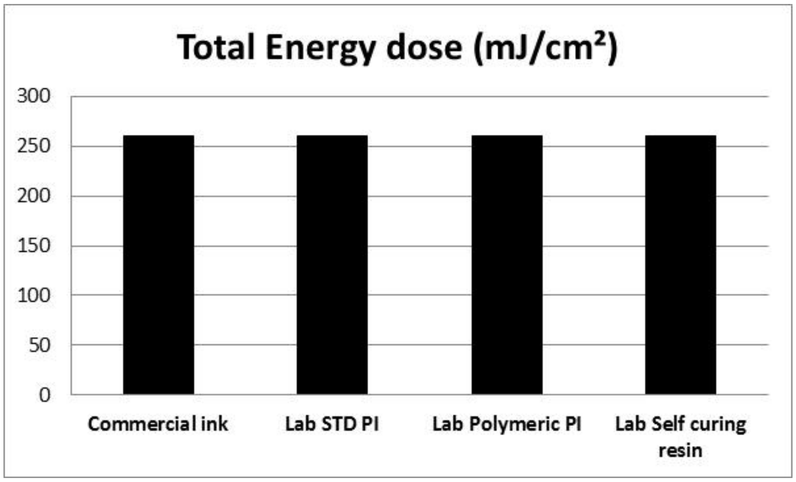

Fig. 8: Reactivity of magenta offset inks: Total energy dose in mJ/cm² to obtain a dry film (1.2 g/m²).

Offset ink rheology is measured by a plate and cone rheometer. We look at the full rheology profile from low shear (ink at rest – in the ink duct) until "high" shear (printing). The ratio low shear viscosity/high shear viscosity is called shortness index (SI). Adjusted to the same printing viscosity, a higher SI indicates a higher low shear viscosity, hence less flowing ink. Results of the four different ink systems are given in Fig. 9. The ink based on the self-curing acrylate resin compares fully with commercial inks and lab standard inks whereas the ink using polymeric photoinitiators clearly lacks flow.

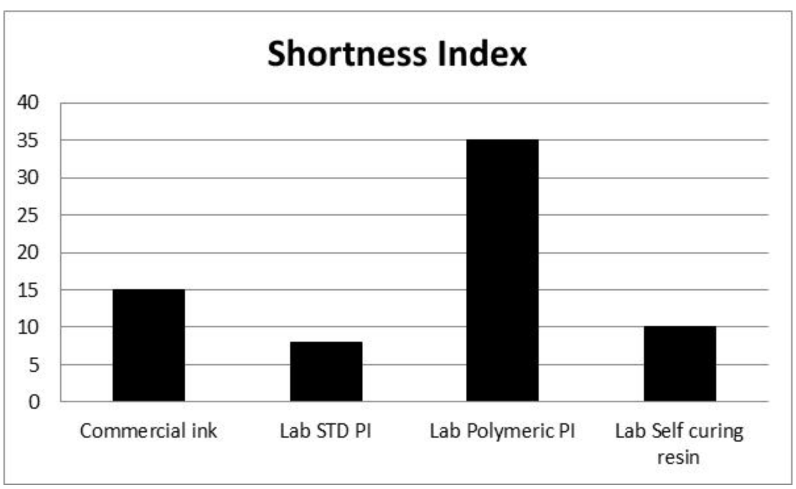

Fig. 9: Ink flow properties: shortness index (SI) of magenta offset inks. SI = ratio low shear viscosity/high shear viscosity.

PACKAGING SAFETY

Printing inks and varnishes applied on food packaging need not only to perform well in printability, providing the necessary chemical and mechanical resistance properties, but need of course to result in low odor and low migration ensuring packaging safety.

While most all regulations relating to food packaging materials around the globe share the same objectives: the protection of food quality and of consumer health, they differ significantly in their practical aspects. The differences amongst regulations combined with the lack of specific regulations on inks in the USA and the EU has resulted in a wide range of usage interpretations and market requirements for the inks. Therefore, below some guidance has been provided through primary applicable regulations in the European Union.

Whilst European harmonized legislation does not specifically cover printing inks, there are some legislative instruments which impact materials and articles intended for direct contact with food.

Europe

The framework Regulation (EC) No 1935/2004 requires in Article 3 that materials and articles in contact with food, whether printed or not, shall be manufactured in accordance with good manufacturing practices, so that under normal or foreseeable conditions of use, they do not transfer their constituents to the food in quantities which could endanger human health; or bring about an unacceptable change in the composition of the food; or bring about a deterioration in the organoleptic characteristics thereof.

The Swiss authorities have issued in 2007 a revision of the Ordinance on Materials and Articles in Contact with Food (SR 817.023.21), which introduces new regulations on packaging inks with a detection limit of 0,01 mg/kg food. Although it is not an EU regulation, the Swiss Ordinance on printing inks rapidly became a market requirement in the entire EU and beyond. It came into effect in April 2010 when the updated list of substances permitted for the manufacturing of printing inks (annex 6) was published. One of the main aspects of the Swiss Ordinance is that packaging inks are only allowed to be manufactured using the substances specified in positive lists. The positive lists are of two kinds. The A list of evaluated substances can be used within the established restriction (e.g. migration limits). The B lists of non-evaluated substances can only be used provided their migration is not detectable with a detection limit of 0,01 mg/kg food.

Germany is currently working on a draft ordinance on printing inks, which is expected to be published in 2014. Although the basic principles are the same as in Swiss Ordinance, the drafts available up to now are showing several practical differences such as the content of the list of evaluated substances, specific provisions on nanomaterials and the fact that the B list of non-evaluated substances is replaced by an inventory list updated and published on their website.

US

In the United States, the use of printing inks in food packaging materials is subject to the laws and regulations administered by the U.S. Food and Drug Administration (FDA). The Federal Food, Drug, and Cosmetic Act ("the act") requires that these materials be manufactured under good manufacturing practices, and that they be safe and suitable for the intended use. In addition to the general manufacturing and safety requirements, the requirements for food additives are also applicable. The FDA defines a food additive as a substance that is “reasonably expected to become a component of food under the intended conditions of use." In most cases, a printing ink – intended for use in a food packaging application in which the ink may reasonably be expected to become a component of food – is considered a food additive. Therefore, its use must be covered by a food additive regulation, an effective Food Contact Notification (FCN), or a Threshold of Regulation exemption letter. Otherwise, the use must fall within an exemption from the need for such clearance. For instance, when a "no migration" position can be properly demonstrated on the basis on appropriate extraction studies or equivalent data, no explicit regulatory clearance will be needed.

China

The Chinese regulations for food packaging materials evolved rapidly in the last year. In September 2008 the "Hygienic Standard for Uses of Additives in Food Containers and Packaging Materials" (GB 9685-2008) was released with the "positive list" of food additives that will be authorized for use in food packaging materials. The implementation date of this new Standard was June 1st, 2009. This standard covers all packaging materials such as plastics, paper, adhesives, coatings and includes the inks.

This standard has been developed with reference to the US Code for Federal Regulations (Chapter 21, Section 170-189), Food Contact Notification (FDA) and EU Directive 2002/72EC. The definition for the Additives covered by the GB 9585-2008 is broad as it includes the additives used to improve the characteristics of the packaging material, the additives used during the production process of the packaging material as well as the monomers and starting substances used to produce it.

The Chinese Hygienic Standard sets up 4 "principles" applicable to the use of additives in food containers and packaging materials. (i) The level of additives and impurities migrating to food should not harm the health of human beings.(ii) The additives migrating to food should not result in any changes of food properties (such as ingredients, structure, color, smell or flavor).(iii) The amount of additives in food containers and packaging materials should be lowered as much as possible.(iv) The additives must comply with the relevant standards of quality and specification.

The positive list that currently contains 959 substances does not cover all the substances used in the various packaging materials under the scope of this regulation. However, in response to the concerns of the industry about the absence of many substances in the positive lists, the Ministry of Health (MoH) initiated in 2010 another round of "grandfathering" (approval of certain substances already approved in other countries without requiring them to go through the complete formal approval process). This exercise resulted in the generation of 3 additional lists of approved substances, containing a total of 559 additives and 107 resins. Any additive not on one of those lists or the use of which does not conform to those specified in the standard, is now considered unlawful and subject to enforcement by Chinese authorities. A process for petitioning new substances has been set up in order to enable manufacturers of food packaging materials to obtain the suitable regulatory approvals.

MIGRATION ASSESMENT

In order to prove compliance of the self-curing acrylate resin with above limitations, it is important to identify and quantify potential migrants. These will be typically unavoidable impurities from starting substances, additives and residuals. To do this, the right analytical tools need to be available and methods developed. Using these “purity indicators”, the raw materials and process to produce our self-curing acrylate resin were optimized. When possible, purity levels –both in raw materials as the self-curing acrylate resin-are set such that in a worst case calculation the SML or 10 ppb cannot be passed. Based on this assessment, it is determined what needs to be measured when performing a migration test.

For a worst case calculation, it is assumed that the formulation is only made up of the self-curing acrylate resin, 6 dm2 packaging is in contact with 1 liter food, the packaging is fully covered with a 3 g/m2 ink layer and the acrylate migrates fully from the print layer to the food (100% migration). A worst case migration in ppb can then be calculated as:

0.06 x 3 x content of component in self-curing acrylate resin (ppm) = x ppb

Migration testing of self-curing acrylate resin:

A simple formulation composed of 70% of polyether tetra acrylate and 30% self-curing acrylate resin was used. Applied at 3 g/m^2 and cured with a 120 W/cm Mercury lamp with a total energy dose of 750 mJ/cm^2.

Ethanol 95% was used as “universal” simulant. The simulant was put in direct contact with the cured film in order to exclude influence of the substrate. Contact time was three days at 40°C. This is of course more a worst case than it is a real time situation.

Analysis of stabilizers/additives, raw materials and acrylates extracted by the food simulant is performed using three different analytical techniques (High-Performance Liquid Chromatography with Fluorescence Detection (HPLC-FLD)), Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography- tandem Mass Spectrometry (LC-MS^n)) depending on the component(s).

Initial results indicate low molecular weight acrylates extraction are below detection limits (ppb level); amount of the self-curing resin extracted is negligible which could be expected given the high molecular weight of around 1000 Dalton.

Given the fact we’re dealing here with extraction rather than migration, the results are very encouraging.

CONCLUSION

Migration of small molecular weight photoinitiators have put the use of UV curing for food packaging in a negative spotlight. Therefore, so called higher molecular weight polymeric photoinitiators were developed decreasing migration risk. These products are often difficult to solubilize in acrylates. A “self-curing acrylate resin” has therefore been developed making it possible to produce UV curable inks and varnishes without the addition of photoinitiators.

Application results show the self-curing acrylate resin can be used in inks using different types of pigments using different application techniques. Raw material and process optimization resulted in an acrylate resin with high purity enabling low migration characteristics.