

RADIATION CURE TECHNOLOGY USED IN INKS & COATINGS

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INTRODUCTION:

Curing by the mean of a radiation source, also called radiopolymerisation is used in Europe since 1972 in the graphic arts industry and found a consistent progress in this field since that period.

What is a radiopolymerisation ?

This is the curing or polymerisation of an ink or varnish which is initiated by a radiation source such as Ultra Violet light or by an electron beam of accelerated electrons (called electron beam curing).

The curing needs to be instantaneous (less than 1 second exposure time) while the ink and coating do not contain any volatile components like solvents. Even the provided energy from the radiation source is only used to initiate the polymerisation and not to heat the substrate or the ink in order to evaporate the water or the solvents.

Advantages:

The radiation cure technology is the only technology who meets the 3-E rules which are: ECONOMY, ENERGY, and ECOLOGY.

ECONOMY:

- Nowadays high production speed is a need for the printer to remain competitive while producing a high quality end-product, radiation cure inks can cure at very high speed (0.05-0.1 second) in comparison with "fast" heat drying inks which dry within seconds while oxidatively cross-linking inks cure within hours.
- Mean while the tendency exist to increase the web speed for offset printing till 700 meters/minute.
- As the inks and coatings are generally solvent or water free, this means that significant lower ink weights are printed.

ENERGY:

The energy which is needed to cure radiation curable inks is only to initiate the radical polymerisation. There is no further need for any energy to drive off solvents or heating the substrate.

The high energy consumption with a low efficiency is necessary to dry conventional inks or to evaporate the solvents, water or mineral oils. Beside that there is consistent increase of energy consumption to incinerate the evaporated oils or solvents as the air pollution regulations become more and more severe.

ECOLOGY:

The relatively high levels of solvents in the conventional drying system provides a high degree of air pollution in case the solvents are not recycled.

Radiation cure systems which are considered as being 100% solids are the exact answer to the pollution problem. More and more countries are implementing severe regulations on air pollution by banning the CO₂-emission which is formed by burning gas or oil, or by banning solvent emission into the air.

1. RADIATION CURABLE PRINTING INKS.

Over the past two decades, enormous progress has been made by the resin, ink and equipment manufacturers in order to respond to the continuous pressure from the printer to increase the output, increase the quality of the printing stock while maintaining price competitive.

- UV-curable or electron beam curable inks and coatings developed during the recent years.

- Letterpress printing inks
- Screen printing inks
- Web offset inks
- Flexographic printing inks
- Clear overprint varnishes

Each of these inks require special resins and diluents. It has been proven for more than 25 years, that the chemicals used in the radiation curable printing ink need acrylic unsaturations in their backbone in order to provide a fast cure respond when lightened by a UV-source. Recent developments show that other chemistry or other cure systems like cyclo aliphatic epoxy resins provide decent printing results.

However, the ethereal dream of the printers is to obtain an ink which remain stable on the printing press, with no viscosity increase on the rollers due to solvent evaporation and which dries immediately after being printed in order to maintain its high resolution. So far this is almost possible with radiation curable inks. The fact radiation cure inks do not contain solvents remain as such stable on the press. Further all the resins present in the ink have a vapour tension of less than 1 mm of Mercury at 60° .

Curing and drying time of the inks is almost immediately after printing once and the ink is initiated by UV-light. Curing completes further at room temperature.

An advantage of this technology is that a wide range of substrates can be printed such as paper, card board, metal and even heat sensitive plastics.

1.1 DIFFERENT APPLICATION

Following list is a summary of substrates which are printed and coated by the mean of radiation curable inks:

- cosmetic packaging (primary and secondary packaging)
- food packaging
- tooth paste tubes (primary and secondary packaging)
- plastic labels
- book and magazine covers
- compact disk
- video disk
- record sleeves
- bank notes, cheques, credit cards
- postal cards, publications, brochures etc..
- business forms
- beer cans and aseptic packaging
- plastic bottles
- printed circuit boards
- skies
- wind shields and dashboards in cars
- ceramic inks and printed glass
- outdoor resistant advertising panels
- computer parts
- plastic or paper shopping bags
- aluminised labels are printed with UV of EB curable inks

Of course this is an incomplete list because it becomes impossible to keep track of all innovations the market requires. It is a fact that the number substrates an articles printed do not decrease.

2. CHEMISTRY

2.1 ACRYLATED BINDERS:

As a printing ink is produced of a high viscous resin part, non volatile reactive diluents, photoinitiators, pigments, fillers and additives, we can classify the resin materials into different chemical families :

- Polyester acrylates
- Urethane acrylates
- Epoxy acrylates
- Acrylic acrylates

The non volatile diluents called reactive diluents are acrylated monomers or diluting oligomers and are used to adjust the final viscosity of the ink and to increase the cross linking density. Photoinitiators and photo accelerators are necessary only to initiate the cure or polymerization of the ink.

The type of photoinitiators used in the liquid ink determines the cure speed of the ink, while the photo accelerator is responsible to overcome oxygen inhibition on the ink surface while exposed to the UV-light and provides as such a faster cure, higher gloss and better rub resistance.

Electron beam curable inks and varnishes have no need for a photoinitiator system.

2.2 CATIONIC CURE RESINS

Apart from paste inks and silk screen inks, low viscosity UV-curable inks gain more and more interest in the printing industry. Because of the need of low viscous oligomers and diluents, the family of cyclo aliphatic epoxy resins can find their use in the liquid printing inks. Even if this chemistry is existing for more than 10 years, it is only in recent years that they found their industrial application in the printing industry. Because of the sensitivity to humidity during curing and to alkaline compositions in the inks, the use of these chemicals can be limited in printing inks.

3. TYPES OF INKS

3.1 LITHOGRAPHIC INKS

While radiation curable litho inks are being used exclusively in Europe, Japan and the USA for many years, acceptance have now been shown in the Asian countries.

Lithographic inks are used in a process which is based on a chemical difference between image and non-image area (in contrast to printing systems with a physical relief difference).

To obtain an image, the lithographic ink needs to be in "competition" with a water solution the so called fountain solution. The ink will go preferentially on to the image area and will be repelled from the non-image area by the fountain solution. This hydrophilic-lipophilic balance (HLB) is critically but important for the ink to function and to remain stable for extended run times.

If the ink is too fountain solution loving, it forms a water emulsion causing dilution and changes in rheology. Even the evaporation of the excessive amount of absorbed water from the ink can cause a lower gloss and even pin holes on the printed ink surface.

On the printing press, the image on the lithographic plate is transferred to a rubber roll which is in contact with the substrate. This indirect printing is also call "offset". The lithographic behaviour of an ink can be measured on a tack-a-scope where tack of the ink is measured after the inks have been in contact and repulsed by the fountain solution.

3.1.1 As the final ink contains 5 to 10 different ingredients attention should be paid to the following points :

- HLB balance
- pigment wetting properties
- low misting properties
- fast cure speed
- good colour hiding
- good print resolution
- exact viscosity
- not being toxic

Resins for lithographic inks must as such fulfil a number of requirements:

(1) The right HLB-balance : -

The hydrophobic character must be high enough to avoid mixing of the fount solution with the ink. The binders must however be able to emulsify small droplets of fount solution on the ink surface.

(2) Good pigment wetting properties : -

The choice of the pigment is very important on the lithographic behaviour of the ink. The type of pigment has not only an influence on the viscosity of the ink but also on its lithographic behaviour. Organic pigment are mostly recommend to be used in litho inks.

(3) Low misting : -

The misting effect of an ink are microscopic ink particles in the atmosphere surrounding the rotating rollers. Good resins as well as the formulating know how can over come this problem.

(4) Good reactivity : -

Because printing presses are running at very high speed, one of the basic requirements of an ink is the cure speed or reactivity. This is the speed (expressed in metres/minute or a number of printed sheets/hour output) required to have the ink completely dried and tack free.

3.1.2 Typical characteristics of a litho ink :

- Viscosity : 5000 - 10000 mPa.s
- Thickness of the print : 2 - 4 g/m²
- Cure speed : 3000 - 5000 sheets/hr
- Not toxic
- Low skin irritation
- Solvent free

3.1.3 The cured ink should :

- adhere to the substrate : paper, board, plastic, metal
- have a good chemical resistance
- have the required gloss
- be over printable by a clear varnish if necessary

3.1.4 Typical starting formulation

Binder system, reactive diluents	60 - 80 %
Pigments	10 - 20 %
Photoinitiators	5 - 15 %
Stabilizers	0.01 - 0.1 %
Additives : fillers	5 - 10 %
waxes	
pigment wetting additives etc	

Because the binders and diluents are responsible for most of the required properties, special acrylated resins have been developed over the last 2 decades.

3.1.5 Recommended binder systems:

3.1.5.1 Reactive diluents:

- | | |
|-------------------------|--|
| - OTA 480 | : oligo triacrylate |
| - Ebecryl 150 | : bisphenol A. derivative acrylate |
| - Ebecryl 160 - TMPEOTA | : ethoxylated trimethylolpropane triacrylate |
| - TMPTA | : trimethylol propane triacrylate |
| - PETIA | : pentaerythrytol tri/tetraacrylate |

P.S. Because of the water sensitivity and the slower cure speed, it is recommended not to use the common monomers like Tripropylene glycol diacrylate (TPGDA) and 1.6 Hexane diol diacrylate (HDDA).

3.1.5.2 Resin systems:

In function of the substrates to print on, different families of resins can be recommended.

a) Paper and Carton

* A combination of:

Ebecryl 1608 and Eb 657 1/1 or 2/1
(epoxy acrylate) (polyester acrylate)

* Ebecryl 3608 > |
> | modified epoxy acrylates

Ebecryl 3702 > |

* Ebecryl 870 (polyester acrylate)

* Ebecryl 450 (polyester acrylate)

b) Metallic and plastic substrates

* Ebecryl 438 eventually combined with Ebecryl 657 (polyester)

3.1.5.3 Photoinitiator systems

As the resins and diluents influences the total behaviour of a litho ink, the photoinitiator part has an important role on the overall ink behaviour.

The photoinitiator which is responsible to initiate the radical polymerization has as the need to be physically compatible with the resin part, able to absorb the UV-light (energy) and to start a photo chemical reaction. In many cases a photoinitiator is combined with other products the so called photo synergist, initiators or sensitizers in order to increase the cure speed, the cure in depth and the surface cure.

The Photoinitiator system used in the ink can influence the physical properties of the cured ink such as :

- surface hardness and cure rate in depth
- chemical resistance of the ink
- yellowness of the printed ink
- abrasion resistance

Typical photoinitiator families used in litho ink are :

- α -Hydroxy alkyd phenones
- Amino alkyd phenones (to over win oxygen inhibition on the ink surface)
- Amino benzoates
- (Acrylated) Benzophenone
- Thioxanthenes
- Benzyl dimethyl ketal
- Morpholines

3.1.5.4 Stabilizers:

Once an ink is formulated and photosensitized, stability or shelf life of the ink can be critical if the ink is not stored under proper conditions, or is abused during manufacturing, or if additives and pigments present in the ink contain impurities.

To overcome these problems, inks can be stabilized by adding small amounts of stabilizers like hydroquinone, methyl ethers of hydroquinone etc....

3.2 FLEXO GRAPHIC INKS:

Flexographic inks and gravure inks can be categorized between the fluid or liquid inks because of their extreme low viscosity of approx. 100 mPa.s. These inks have been traditionally solvent based at about 20-30% solids content. However, regulatory pressure on the use of solvents are making it necessary for the printing industry to evaluate the more environmental friendly technologies.

Waterborne flexo inks have made inroads but still suffer from printing quality problems and the recyclability of printed paper. In additions the VOC-problem is not completely eliminated due to the presence of co-solvents in the ink.

About 4 years ago, the 100% solids UV-curable flexo inks started to replace the conventional water based and solvent based flexo and gravure inks.

Since there is no solvent/water evaporation that can lead to drying on the printing plates, higher print quality and easier press operations are expected. In addition, there is less waste. Despite these advantages, development of UV-flexo inks has been slow to evolve, primarily due to viscosity limitations. UV curable oligomers are generally high viscosity. Thus, making a flexo ink with good hiding (high pigment concentration) and printability (rheology) has been difficult. These limitations have been largely overcome in recent years. Modifications of flexo presses such as new doctor blade. Systems and modified anilox rolls have allowed utilization of higher viscosity inks. Significant advances in the chemistry of UV curable raw materials have also helped make UV-flexo a reality.

Nevertheless, if the modifications on the flexo press are not yet acceptable to the ink viscosity, the use of water as a diluent for an acrylated resin system can be recommended. In many cases, where water is used in an emulsified form the viscosity reduction within the market existing acrylated resins is not sufficient to overcome the printing problems.

New generation of acrylated binders have been developed recently where water is used as a real diluent without the need of any organic co-solvents. This ink system allows already the production of a low viscosity ink with good opacity, high cure response and long term stability. Further the printed ink requires no water flash off prior to curing.

3.2.1 Requirements of the liquid flexo ink

- Low viscosity
- Good pigment wetting properties
- Fast cure speed.
- Good printing properties with good resolution.

3.2.2 Properties of the cured ink such as :

- Good adhesion to a wide variety of substrates
 - paper
 - polyester foil
 - polyethylene / polypropylene
 - PVC, etc...
- Good flexibility when printed on flexible substrates.
- High gloss and print resolution.
- Good surface hardness

3.2.3 Typical starting formulation:

Pigment paste	40 - 50 %
Let down vehicle	40 - 50 %
Photoinitiator system	5 - 10 %
Additives	1 - 10 %

3.2.4 Recommended oligomer systems:

a) Pigment paste:

EBECRYL 657
EBECRYL 450
IRR 182
OTA 480

grinded with 25 % pigment in presence of pigment wetting additives.

b) Let Down Vehicle:

EBECRYL 81	polyester acrylate
EBECRYL 82	polyester acrylate
EBECRYL 8402	aliphatic urethane acrylate
OTA 480	oligo triacrylate
TMPTA	trimethylolpropane triacrylate
EBECRYL 160 (TMPEOTA)	alkoxylated trimethylolpropane triacrylate
DPGDA	dipropyleneglycol diacrylate

A third family of resins which can be recommended for the use in liquid inks are the cationic curable systems. These cyclo aliphatic epoxy resins have as main property that the cure is not inhibited by oxygen on the printed ink surface, which means that low levels of photoinitiators can be used with as result that they give a low residual odour after cure.

Typical characteristics of the cationic cure systems is the low shrinkage they provide during the curing which improves the adhesion to the so called difficult substrates in comparison to the fast cure and high shrinking UV-curable acrylated systems.

Anyhow these advantages do not always compensate other drawbacks such as the sensitiveness to certain organic bases present in pigments or additives and the sensitivity to the humidity present in the air which inhibits the polymerization or cure of the ink. It is a fact that the cationic curable systems find their use in certain application like metal and plastic printing if the proper environmental conditions or the humidity levels in the air are respected (humidity levels of above 60% can strongly inhibit the polymerization).

A main break through in the flexo printing occurred about 5 years ago. In cooperation with the equipment manufactures who were able to modify the printing presses, ink manufactures in Europe and the USA were able to produce 100% solids UV-curable flexo inks used for printing paper board, plastic labels, bags etc.

These inks are based for 100% on acrylated diluents and oligomers, combined with the photoinitiating systems, pigments and additives, they provide excellent print quality, high gloss and high resolution.

The main interest for the 100% solid flexo or gravure inks are a number of unexpected advantages which appeared during the daily experience such as:

- (1) Improvement of the printing quality
- (2) In contradiction to the water and solvent based inks, the UV-inks are not sensitive to humidity changes, temperature changes, pH and speed of solvent or water evaporation.
- (3) Adhesion to plastics.
- (4) Potential for long and short range print jobs because of the short time necessary to adjust and cleaning the printing press. As a consequence, less waste will be produced.
- (5) UV-cured flexo inks show better chemical and abrasion resistancy as well as a better light resistancy.

3.3 SCREEN PRINT INKS

It is not clear where to categorize the screen inks. Generally the viscosity is too high for being a liquid ink and too low for being a paste ink. Where the film weights for offset or flexo printing generally do not exceed 5 g/m², UV-screen inks are printed at layer thicknesses between 6 and 30g/m².

UV technology has made a major contribution in the area of overprint varnishing and polythene bottle printing. Its growth into general display screen printing has been more modest but it is now being accepted by the industry as offering many advantages over solvent based inks and with the increase in 4 colour process printing, UV has really found a niche.

Environmental considerations have also altered the industry's attitude to UV. Pressures to reduce solvent emissions and concern about health and safety have both been instrumental in advancing the use of UV in screen printing. Developments, such as conventional water based inks, have been found to have serious technical limitations which has made UV the only realistic alternative to achieving a cleaner environment.

UV curing has been found to offer many benefits to the screen printer and its advantages in screen printing are probably greater than those found in any of the other printing processes. A great advantage of UV curable inks in screen printing is undoubtedly that of screen stability. UV inks contain no volatile components. Therefore, they will not dry in the mesh. The closure of mesh apertures leads to a loss of print quality and necessitates frequent stoppages for wash-up.

The excellent screen stability obtained by using UV inks also allows much finer detail to be reported and this has been of particular benefit in 4 colour process printing. The speed of cure achievable with UV systems is an important advantage over solvent based inks and higher production speeds can be obtained. This has been of considerable advantage in such area as overprint varnishing, where line speeds of 70 metres per minute are not uncommon at 3,500 impressions/hour. Label printers have also benefitted from increased production speeds, due to the rapid curing of UV inks.

To many screen printers a major advantage of UV inks and varnishes is probably the greater film weight obtained, which enhances the three dimensional quality of the print. Corresponding levels of gloss are also higher than those conventional screen inks and this has been particularly beneficial in the decoration of polythene bottles, where the improved visual impact is very noticeable.

Savings in energy have been reported in the use of UV inks over conventional hot air drying systems. Such savings are difficult to quantify, but they have been claimed to be up to 50% of a jet air dryer running continuously at print speeds in excess of 3000 impressions per hour.

Space savings are obvious, as a UV lamp system is a fraction of the size of a thermal oven. Polythene bottle printers have found considerable advantages in the much smaller size of the UV dryer compared with the huge elevator basket dryers which operates at 80°C and take up to 10 minutes for the ink to be fully cured.

A major disadvantage of UV curable screen inks is that there are limitations to the opacity of the inks, but developments in photoinitiators and special developed oligomers and monomers mean that much higher density inks are now available. Screen inks are applied in much thicker films than those from the other printing processes. For good hiding power, high pigment levels are desirable. Pigments tend to compete with photoinitiators for the incident UV radiation and use of certain types of pigment is, therefore restricted.

The fast curing of free radical UV materials does involve shrinkage of the ink or varnish film and this sometimes results in the adhesion to non-porous substrates being inferior to that of a slower drying conventional ink. Great improvements have, however, been made in the design of oligomers so that this is not such a great problem as it was.

3.4 Electron Beam Curable Inks

Printing inks cured by the mean of accelerated electrons instead of Ultra Violet light found its first industrial application approximately 10 years ago.

Since than, printing (wet offset) and coating of aseptic packaging for food containers is successfully done in Europe, the USA and in some parts of Asia. Because these inks and coatings are used in application such as indirect food, it means that special attention need to be paid while formulating the ink.

The main characteristics for such products are the extreme low levels of residual extractables and residual odour after curing which need to be guaranteed by the supplier of the ink.

Line speed of EB-curable inks are similar as the UV-curable inks. The main difference of EB-curable inks versus the UV-inks is the presence of a photoinitiator system. These are not necessary for EB-inks and coatings. Photoinitiators do generally not participate in the curing and are responsible for high levels of extractables and residual odour after curing. These extractables and odours are transferred into dry or liquid food and change the taste.

Now a days electron beam curable inks and coatings are clean because a precise selection of pigments, additives and radiation curable resins have been specially developed for this applications. Resins suppliers have to guarantee levels of < 10 ppm of residual solvents in the resins and diluents. Such resins became commercial available over recent years in order to allow the ink manufacturer to produce an ink which complies with the regulations set up by the packaging manufacturer.

4. HEALTH AND SAFETY

For many years, the radiation cure technology has been criticized for its health and safety aspect. Some of the most important critics about the acrylated resins used in printing inks are the so called toxicity and irritation effects on people's skin. In deed, in the early years there were some acrylate monomers which were formed to be potential skin irritant or toxic, but their use has been discontinued.

4.1 TOXICITY

The toxicity is defined by lethal doses (LD50) oral or dermal. In many cases it has been proven that the majority of radiation cure resins are not considered for being toxic. The table in annex shows the LD50 oral and dermal values for the most for coming oligomers and monomers supplied by our company. On a comparison, the lethal dose of the drug acetyl salicylic acid and kitchen salt (NaCl) are more toxic than any of the acrylated resins.

Even the very contested monomers like 1.6 Hexanediol diacrylate (HDDA) and Trimethylol-proprane triacrylate (TMPTA) are considered as not being toxic. It is further worth to mention that these products have a vapour tension of less than 1mm Mercury at 60°C, and such the danger for inhalation by evaporation is practically neglectable.

4.2 SKIN IRRITATION

It is well known that acrylated resins have a potential skin irritating effect. Oligomers are generally less irritant than the monomers. First generation monomers like HDDA and TMPTA have shown for being more skin irritant than the second generation monomers which are alkoxyated monomers.

Generally ink manufacturers avoid the use of skin irritating products if it is possible, but some of these products provide exceptional good properties such that their use is mandatory to produce a high quality ink.

The primary skin irritation index is measured following 2 methods :

The primary skin irritation index (PII) expressed in a Draize value, and there is the skin irritation according to the OECD method.

4.2.1 DRAIZE VALUE

To determine the primary skin irritation index, the liquid product sample is brought in contact to the **fur free skin of a rabbit, intact and abraded during 24 hours**. According to the aggressiveness of the product, the skin becomes red, swollen or shows blisters.

4.2.2 OECD-Method

To determine the skin irritation value according OECD method, the liquid product sample is also brought in contact with **fur free skin of a rabbit but only to the intact skin and not the abraded part, for only 4 hours**. Because this test seems to be more realistic for extrapolations to the human skin, the industry now a days pays more attention to the skin irritation value according to the OECD method than the primary Draize skin irritation index.

The irritation index is as such classified into 4 categories :

Index :	0	=	non irritant
	0-2	=	slightly irritant
	2-5	=	moderately irritant
	5-8	=	sever irritant

As an indication, the majority of oligomers and reactive diluents used in the radiation cure applications have a Draize index of less than 3 or OECD-value of below 2, while the famous solvent "white spirit" shows a Draize value of 6 which means severe irritant.

It is evident that these resins, even if they are non irritant or hazardous need to be handled with care. All contact with eyes and skin need to be avoid and proper training for the workers needs to be arranged prior using the products.

It is important to notify that all toxicity and irritancy information is obtained on the liquid resins, before curing or before they become in a solid state. After cure the coating or ink becomes even less toxic and not irritant.

Radiation cure inks are now applied for more than 22 years so far nobody has been intoxicated by manipulating or handling objects printed by radiation cure systems.

CONCLUSIONS

The photopolymerisation is in a continuous evolution. One technology never replaces completely another technology, but the tendencies such as:

- the solvent emission in the air has to be reduced
- regulations about the handling of chemicals become more and severe
- we have to save on energy
- the use of dangerous chemicals needs to be reduced
- there is a need for quality improvement

are practically irreversible

This does not means that all solvent based inks and coatings will be replaced by radiation curable inks, but they will be replaced where it is possible.

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