UV curing Flexographic Inks a formulating concept

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Introduction

The flexographic process
Flexography is a process in which the printing image stands up in relief. A liquid ink (a generic term used for low viscosity inks) is used which may be solvent-based, water- based inks or UV-curing. UV-cured systems have seen rapid growth in certain segments of the flexo world especially in the area of mid size presses and narrow web printing for labels. The process has several distinctive features that must be considered when formulating suitable UV curing inks.

Press configurations
There are three basic configuration types for flexography presses:

- stack;
- common-impression;
- In-line.

The first two are the more common for solvent and water based systems and UV curing flexo inks have made some in-roads here but the inline press has become the major press configuration for the printing of UV curing flexo inks. .

The Printing unit
The functions of the inking system is to meter out a fine and controlled film of liquid ink, and apply this to the surface of the printing plate. Low viscosity inks are required that transfer rapidly and uniformly, thus enabling fast printing speeds to be achieved on non-absorbent materials such as films and foils.
UV curing Flexo inks are usually in the range of 1.0 Pascal/sec in viscosity. Although some users believe it would be better to have lower viscosities it is more important to have a balanced series of inks where the viscosities of each ink are similar to each other. Cure or running speeds have increased as Press manufactures have improved their design and speeds of over 200 m/min our now possible.

Anilox
The application of ink to the surface of the printing plate is by means of a screened (Anilox) roller. The result is a simple ink feed system when compared to the complexity of a Litho press and does not have the complexities of ink water balance. However, the process has its own unique requirements for physical characteristics, rheology and transfer properties. This is especially true for the UV inks now being used. The anilox roller is a crucial factor in achieving good quality flexo printing and there is still much to be learnt from a UV curing ink perspective. Ceramic rollers and chrome plated rollers can carry very different amounts of ink when such factors as cell volume, geometry and screen size are considered. These factors are even more critical in the success of suitable UV curing inks because of the different surface energies and physical parameters compared to traditional solvent based inks. Much

work has been carried out to determine the optimum anilox and plate combinations for use with UV ink and many suppliers of machine, anilox and plate have specific recommendations for UV inks.

Doctor blade

The doctor blade removes the excess ink from the surface of the anilox as the ink is transferred to the flexoplate. For high-quality printing, reverse angle doctoring using nylon, polyester or ultrahigh molecular weight polyethylene have replaced steel which gives less anilox wear. On a number of UV curing presses an ink chamber formed by a double doctor system is used which has provided a totally enclosed inking system that has shown greater benefit for the efficient transfer of UV curing flexo inks.

Flexoplate

The plates consist basically of light-sensitive photopolymer, which when exposed to UV light through a photographic negative, polymerizes and becomes resistant to the washing-out medium. The chemistry of the plates is similar to the UV inks in some aspects and care should be taken to avoid damage of the plates from the UV ink chemistry. The main areas of concern are with the selection of the low molecular weight content of the ink such as monomers and some additives. Flexoplates as with the Anilox should be selected to perform with UV curing inks

New presses

The units of modern flexographic printing presses are now engineered to very tight tolerances. The ability to manufacture to these standards, in combination with the development of higher print quality UV curing inks, has contributed to the growth in flexographic printing, and its use for higher-quality products than was previously possible.

Typical UV-Flexo applications

UV curing Flexo inks were introduced originally for the printing of labels and have now become the dominant technology in that field. In the 90s a number of wide web machines (>100 cm) were converted to UV curing but the real growth came later in the mid-size (60 to 100 cm) printing machines

The popularity of UV flexo printing inks and varnishes is high and still rising. One good reason is the freedom from solvents which reduces emissions and probably one of the original reasons to use UV curing technology. However, these products also offer superior print quality with no solvent replenishment and rapid readiness for use, good adhesion on flexible and many other substrates, high chemical and product resistance and high running speeds also means that UV/EB-cured inks are now being considered in many printing areas. UV curing Flexo inks are now printing on nearly all the ranges of substrates used for finished products such as yoghurt tops and cups, sugar, soup and spice sachets, flexible packaging, milk and juice cartons, pet food packaging and even cigarette packs.

Flexographic Ink Formulation

A basic UV curing flexograhic ink contains:-

Pigment
Oligomer
Monomer
Photoinitiator
Additives

The following tables show the products considered in this paper for the development of a UV curing flexo ink series.

Oligomer

Grinding Oligomer

Grinding vehicles are essential in the development of flexographic inks. These vehicles will efficiently break down pigment agglomerates and will allow for efficient stabilization. Using these vehicles will increase flow, stability, and colour development of the ink.

Product Code GENOMER	Structure	Properties
3611	Polyster Acrylate	Excellent pigment wetting, fast cure speed
2280	AR Epoxy Acrylate	Good pigment wetting, excellent toughness
2255	AR Epoxy Acrylate	Mid viscosity, good reactivity and toughness
2259	AR Epoxy Acrylate	Low viscosity, good reactivity and toughness

Letdown Oligomers

Letdown Oligomers provide enhanced physical properties, cure speed, and adhesion.

Product Code GENOMER	Structure	Properties
1122	AL Urethane Acrylate	Excellent flexibility and adhesion, low odor
2235	AL Epoxy Acrylate	High reactivity, hard films
3364	Polyether Acrylate	High reactivity, good flow
3497	Polyether Acrylate	High reactivity, good flow
3414	Polyether Acrylate	Very high reactivity, good flexibility
PESTA 03-849	Polyester Acrylate	Good reactivity, flexibility and hardness
4590/PP	AL Urethane Acrylate	High reactivity, low yellowing
4622	AR Urethane Acrylate	Very high reactivity and hardness
5142	Acryl. Amine Synergist	Highly improves reactivity and surface cure
5161	Acryl. Amine Synergist	Highly improves reactivity and surface cure
5275	Amine Acrylate	Highly improves reactivity and surface cure, good flexibility and adhesion

Monomers

Monomers are typically used in flexographic formulations at 30 to 60 weight percent of the formulation. Choosing the correct monomers for use is critical. The incorrect type of monomer can lead to plate swell and registration issues. Monomers provide lower viscosity, improved adhesion and contribute to cure rates. Some suggested monomers are shown in the table along with the performance properties they provide.

Product Code MIRAMER	Structure	Properties
M202	HD(EO)3DA	Low viscosity
M216	NPG(PO)2DA	Low viscosity, pigment grinding capabilities
M220	TPGDA	Low viscosity
M222	DPGDA	Low viscosity
M240	BPA(EO)4DA	Increase cure speed and scratch resistance
M300	TMPTA	Increase cure speed and hardness
M3130	TMP(EO)3TA	Increase cure speed and hardness
M320	GPTA	Increase cure speed and hardness
M360	TMP(PO)3TA	Increase cure speed, pigment grinding capabilities
M4004	PPTTA	Increase cure speed and hardness
M410	DiTMPTA	Increase cure speed and hardness
M420	PETTA	Increase cure speed and hardness
M600	DPHA	Increase cure speed and hardness

In-can Stabilizers

In-can stabilizers are an important part of a UV curing flexo ink. They significantly improve shelf live and the stability of the ink during the grinding process.

Product Code GENORAD	Properties
16	Highest efficiency for grinding and storage
18	High efficiency for grinding and storage
20	Stabilizer for clear coatings and pale shades
21	Stabilizer for UV-metallic inks

Photoinitiators

The full range of photoinitiators can be used in UV curing flexo inks but selection will be dependent on the end product requirements. Some suggested photoinitiators are shown in following table.

Chemical identity	PI class	Properties
Benzophenone	Type II	Versatile use in all color shades. Very efficient in combination with synergists.
1-Hydroxy-cyclohexyl-phenyl-ketone	Type I	Used in the PI cocktail as a co-initiator to balance the through and surface cure
Dimethyl-hydroxy-acetophenoe	Type I	Used in the PI cocktail as a co-initiator to balance the through and surface cure
Ethyl-4-dimethyl-aminobenzoate	Synergist	Synergist (H-donor), improves reactivity of systems with Type II photoinitiators
Isoproylthiocanthone	Type II	Very broad absorption range for use in dark and thick ink films.
4-Phenyl-benzophenone	Type II	Efficient benzophenone derivative in combination with synergist.
Alpha-aminoketone	Type I	Absorbs light above 300nm. Efficient through curing of the printed film.
Polym. Aminobenzoate	Synergist	Low odor and migration inks. Properties similar EPD
Polym. Benzophenone	Type II	Low odor and migration inks. Properties similar to BP
Polymeric Thioxanthone	Type II	Low odor and migration inks. Properties similar to ITX
Alpha-aminoketone	Type I	Absorbs light above 300nm. Efficient through curing of the printed film.

Additives:

There are many additives used in the manufacture of UV curing flexo inks. The variety of products that are available on the market makes it difficult to given even a rough overview. Note: successful formulation will often contain quite complex combinations of these additives that must be optimised for the end formulation and requirements.

Application	Product Name	Supplier	Comments
Dispersing Agent	Disperbyk (various)	BYK	Good all rounder products
Dispersing Agent	Solsperse (various)	Lubrizol	Must be accurately used
Defoamer	IP Alcohol	(various)	Small amounts good against macro foam
	AK 350	Whacker	Good against micro foam
Levelling Agent	Dynoadd FI	Dynea	Wetting or flow out aids
	Tego foamex 810	Eyonik Tego	
Slip Agent	DC 57	Dow	Standard silicone
	Tego-glide 435, 450	Eyonik Tego	Good compatibility
	Polyfluo 190, 540	Micro powders	Wax with good compatibility in UV systems
	Ceridust 3620	Clariant specialities	
Anti-dive	Ethocel 4cps	Dow	Used to prevent absorption (dive) into absorbent substrates
OB	Uvitex OB	Ciba	Optical brightner

UV curing ink formulations

The following inks were formulated by preparing an optimal mill-base and then let down to the final finished inks by the addition of monomer, oligomers, photoinitiators and additives. This method allows for the optimum grinding and milling of the pigments without the danger of reactive photoinitiators and sometimes poor grinding oligomers and additives that are required in the final ink. The production of concentrated bases also allows for a number of different ink series to be produced by simply altering the let down formulation. The final formulations shown in this report have been deigned to be a general purpose series.

Mill-bases

The mill-base is the first step, and most crucial, in making a UV flexo ink from a platform manufacturing system. An optimum mill-base will have the maximum amount of pigment dispersed while still maintaining a processable viscosity and rheology. The pigments chosen for this report where available in the Rahn Radlab and have been used for the evaluation of our products in the past. However, pigment selection is the first and some say most important step in the manufacture of UV curing inks. The pigments used here are only a starting point suggestion and it is strongly recommended that a thorough search be carried out to determine the optimum pigments for a particular customers needs. The mill-base formulations shown here can be used as benchmark formulations for the evaluation of alternative pigments. The dispersant used in the mill-base was chosen to compliment the grinding Oligomer G* 3611 used to provide pigment wetting and improved grinding properties. The dispersant additive is not required in the Cyan and White.

The mill-bases were produced on a Bühler SDY-200 mill, with one loose pass at 15 bar followed by up to 3 passes at 20 bar to achieve a fineness of less than 5 micron with no peppers.

[%]	Yellow	Magenta	Cyan	Black	White
Pigment	**PY 13**	**PR 57:1**	**PB 15:3**	**PB 7**	**PW 6**
Supplier Code	**Irgalithyellow LBG**	**Irgalithrubin L4BD**	**Irgalithblue GLO**	**Special black 250**	**Titan 2310**
Supplier	**Ciba**	**Ciba**	**Ciba**	**Degussa**	**Kronos**
Pigment	**35.00**	**35.00**	**35.00**	**35.00**	**50.00**
Genomer 3611	**60.00**	**60.00**	**64.00**	**60.00**	**49.00**
BYK 168	**4.00**	**4.00**	**-**	**4.00**	**-**
Genorad 16	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Viscosity and flow Properties
The viscosity and flow of a mill base or finished inks can be determined by sophisticated measurement on a variety of rheology machines, quickly determined by a cone and plate viscometer or simply and visually shown by the flow plate method.
In this study we have used:
An Advanced AR 550 Rheomat from TA instruments to determine the rheology curves and viscosity of the bases.
A RM 260 Rheomat from Mettler for a QC viscosity check of the inks.
A flow plate method to observe the flow characteristics.

The flow plate method is a simplistic and comparative method where depending on the product 5g to 10g are placed on a glass plate, allowed to settle for 30 sec and then the plate is placed upright at 80°. The length of flow is measured in mm after 1 to 3 minutes depending again on the products being compared i.e. finished ink or mill-base. The Flow, viscosity and rheology curves of the bases have been compared to bases made from a standard Epoxy Acrylate (EPAC) reduced in TMP(EO)3TA.

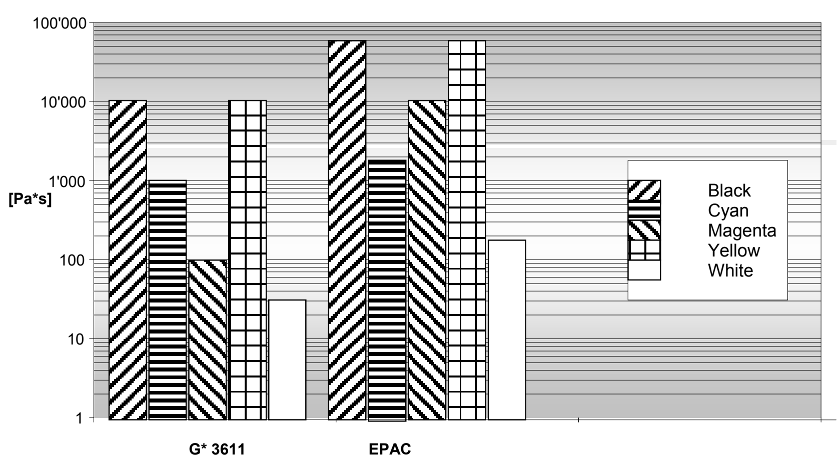


Fig 1. Viscosity of Bases TA AR550 at shear stress 10 pa (oscillation)

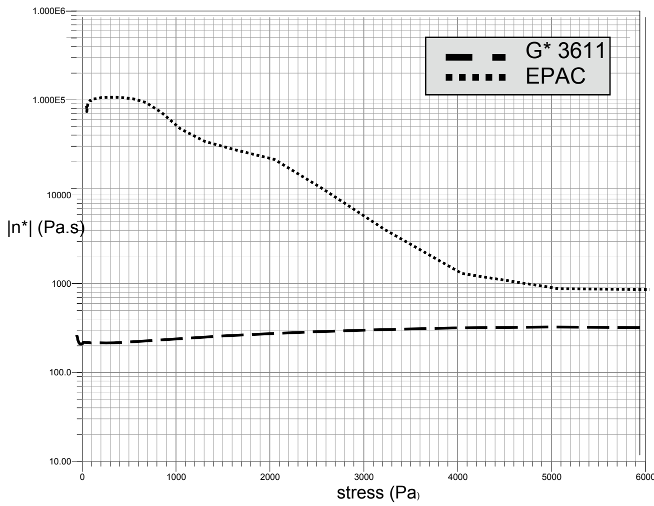


Fig 2.
Rheology curve Magenta base TA AR550 measurement

Flexo Inks

The mill-bases are let down with monomers, oligomers, photoinitiators, and additives to produce the final ink. By varying the letdowns, many different inks can be made from the same mill-base. The let down oligomers and monomers have been selected to give the finished ink properties. The photoinitiators are shown in break-back quantities but are added to the letdown as a eutectic mix.

A break-back of the final ink formulation can also be produced as an in-situ formulation run on a pearl mill such as Buhler K8 but care may be needed with the correct cooling of the mill and/or the eutectic photoinitiators mix left out of the grinding stage and added in the final potting stages.

	Yellow	Magenta	Cyan	Black	White
Mill-base [%]	40.0	42.0	40.0	30.0	52.0
*Magenta				*3.0	
**Cyan				**7.0	
GENORAD* 16	0.5	0.5	0.5	0.5	
GENORAD* 20					0.5
GENOMER* 2259	9.5	9.5	13.5	10.0	10.0
GENOMER* 4622	5.0	5.0	5.0	5.0	
MIRAMER M410					9.0
MIRAMER M3130	15.0	15.0	11.0	18.5	7.0
MIRAMER M220	21.4	19.4	19.5	15.0	12.9
Uvitex OB					0.1
WAX OR SLIP ADDITIVE	1.0	1.0	1.0	1.0	1.0
GENOCURE* EHA	1.9	1.9	2.4	2.5	2.0
GENOCURE *CPK					3.0
GENOCURE* ITX	0.8	0.8	0.9	1.0	
GENOCURE* PBZ	1.9	1.9	2.4	2.5	1.0
GENOCURE*TPO					1.5
IRGACURE 369	3.0	3.0	3.8	4.0	
Total	100	100	100	100	100

	Yellow	Magenta	Cyan	Black	White
Reactivity speed achieved in meters. 1 pass 240 w/cm lamp	**100**	**100**	**100**	**100**	**100**

Viscosity of inks measured on the Mettler RM260

	Yellow	Magenta	Cyan	Black	White
Viscosity [Pa*s @ 25°C]	**1.01**	**1.03**	**1.03**	**0.9**	**0.7**

Please note that the reactivity and viscosities achieved have been part of the ink series design for a balanced series of colours. Lower viscosities can be achieved with some colours but are often counter productive if not in balance with the rest of the colours when run on a press configuration.

Fig 3. Glass plate flow measurements in mm.

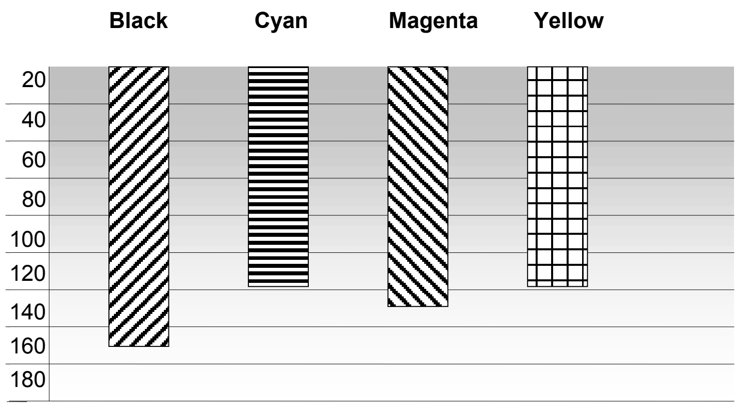
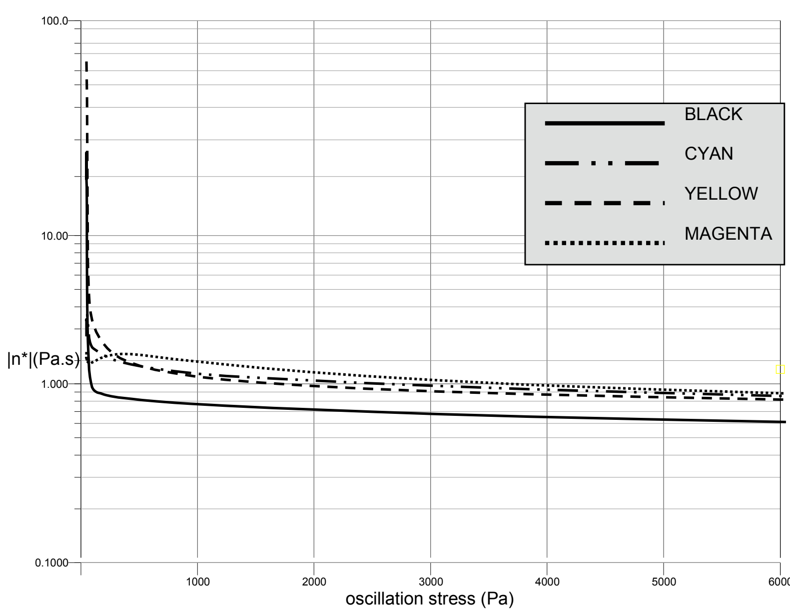


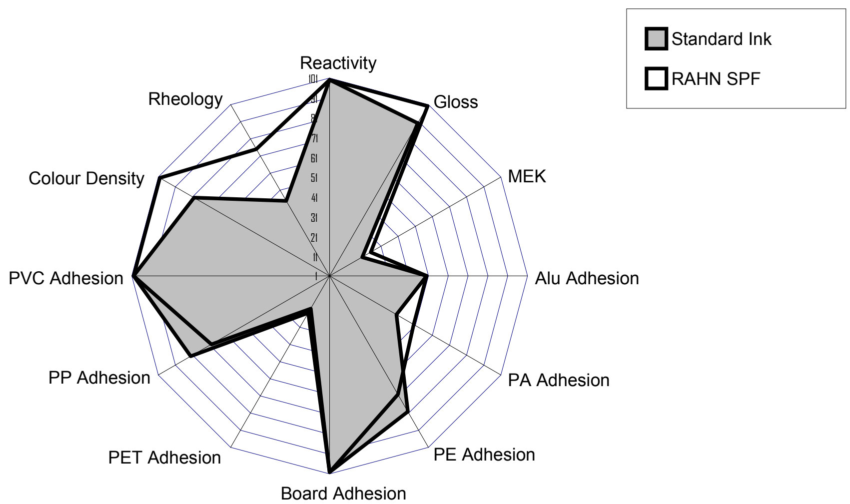
Fig 4. Rheology curves measured on the TA AR 550



The results shown in the flow and rheology measurements are an indication of how the inks will perform on the press. Different presses will have different shear characteristics in the ink train but also in the ink delivery. Some presses may have an enclosed recycling of ink or may have a simple gravity fed flow pan. Usually the better the flow (especially at low stress) the better the performance of the inks on the printing press.

The finished inks were compared to a standard ink series of UV curing flexo inks. The spider diagram below shows some of the properties compared.

Fig 5. Major Properties of RAHN SPF versus Standard ink



Conclusion

The aim of this report was to give the reader an overview of the flexo ink printing process and the requirements needed to develop a UV curing ink series for to-days flexographic presses.

The Rahn Starting Point Formulations represented in this paper form a robust all-round ink series that has excellent reactivity, well balanced rheological properties and good colour strength. It can be used as the foundation or starting point for other ink series where the let down combination can be varied to provide specific properties or improved adhesion on some substrates.