UV Lithographic Inks from self –photoinitiating resins for food packaging applications

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Abstract:
Self-Photoinitiating resins have been developed specifically to meet the demanding product performance needs of offset printing inks. Unique resin design capability through the Michael addition reaction produces acrylic functional resins with outstanding pigment wetting, providing very high quality inks. The hydrophobic/hydrophilic balance of the resins has also been tailored through rigorous resin design. The product resins are self-photoinitiating, yielding the excellent cure efficiency and low extractables necessary for packaging applications. Resin design, properties and performance of offset ink formulations along with migration/extraction data of these novel resins are discussed.

Introduction:
Narrow web has become the process of choice for label printing. Within this; ultra-violet (UV) is the dominant curing technology in flexo and offset printing due to advantages in print quality and converting efficiency. Increasing scrutiny by governments and regulatory agencies around globe regarding food safety and environmental issues is impacting the choices made by converters regarding print processes and technology. This requires careful consideration to be made of the many factors affecting the fitness for use in printing labels and packaging for food. Different types of food packaging and labels have different interactions with the food they are designed for aesthetics or protection. Some examples of the different packaged food type categories are aqueous, acidic, alcoholic and/ or fatty foods. End use risk assessment is a necessary condition in evaluating print technology options. Potential for migration of ink and packaging components as well as environmental contaminants should be significant part of any risk assessment process. The phenomenon of the migration of material into packaged contents is not new, but is currently discussed. Ink systems are not the only possible source of migration, the other sources of migration of contaminants should be carefully considered, and examples are contaminants from substrates, printing press, storage conditions, sanitation and other environmental conditions are all to be considered as total risk assessment process.

When the labels or printed packaging is not in direct contact with the food or protected by a barrier the risk of migration of contaminants is reduced, however when the food is in direct/indirect contact with the printed package and/or label then a complete risk assessment for migration and other factors becomes necessary to comply with regulatory requirements and to protect/preserve the quality of food through it's life cycle.   Some examples are shown below.

Basic situations of printed/coated materials in contact with food
1. Printed layer is separated by a barrier, example: Metal cans
2. Printed layer is a plastic – example, Yogurt containers
3. Printed layer is a flexible multilayer film- example, Cheese packaging, ready to eat dinner trays, etc.

Synthesis of Resin – Chemistry & Resin Design Flexibility

From a design perspective, the technology is broad and readily lends itself to the preparation of novel acrylic materials. The self-initiating resins are formed by the Michael Addition reaction of a Michael donor (e.g. ethyl acetoacetate) with a Michael acceptor (acrylate) in the presence of a basic catalyst. Figure 1 shows the synthesis of a multifunctional acrylic resin in which TMPTA is combined with EAA in a 2:1 ratio to form the tetra functional product. In the synthesis of these novel oligomers, the acrylates utilized can be of any functionality (e.g., monoacrylate, diacrylate, triacrylate, etc.) or of any class (e.g., acrylic monomers epoxy acrylate oligomers, urethane acrylate oligomers, polyester acrylates, etc.). Also, combinations of the above mentioned acrylate building blocks can be used to generate materials with a blending of the structural features and performance characteristics of each of the components.

The choice of starting acrylate(s) allows for the synthesis of resins with defined functionality and architecture. For example when TMPTA ($f = 3$) and dipropylene glycol diacrylate ($f = 2$) are combined in a 1:1 molar ratio and reacted with ethyl acetoacetate, the resulting material will have an average functionality of 3 with one acrylic double bond remaining from the starting diacrylate and two from the starting triacrylate. This design control extends to other monomers and oligomers as well where the functionality and equivalent weight can be tailored by choice of starting material. Molecular weight of the desired product can also be varied and controlled by the choice of Michael donor and Michael acceptor, and the reactant ratio used in the synthesis.

Figure 1. Example Synthesis of a 4-functional branched oligomer.
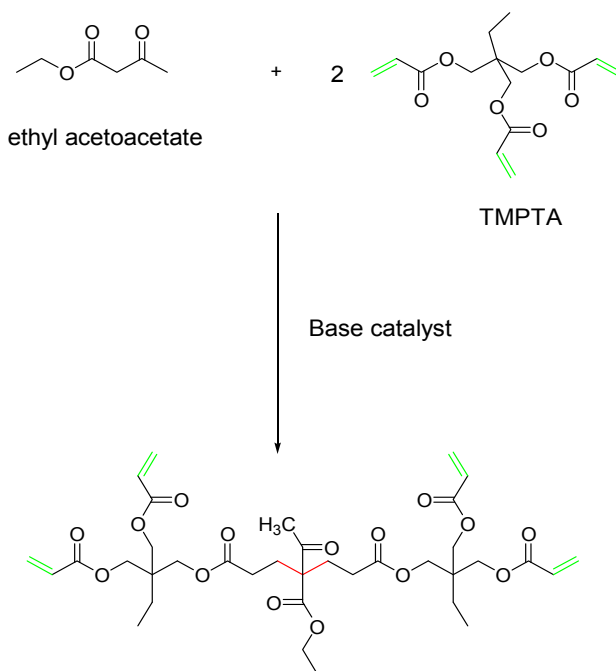
Beyond the broad resin design flexibility, the most outstanding performance feature of these resins is the fact that they "self-cure" upon UV irradiation and physical characteristics, can be tailored (Examples Viscosity, Surface tension). The dose needed to cure the un-pigmented neat resins without

photoinitiator ranges from less than 100 mJ/Cm^2 to 3000mJ/ Cm^2, depending on selection and structure of the starting materials. Low levels of added photoinitiator can reduce dose to tack-free cure even further. UV curing under Nitrogen is also a viable option. Nitrogen blanketing allows UV curing to proceed without inhibition by Oxygen resulting in faster and efficient cure and further lowering migration potential.   Electron beam (EB) curing is also possible with this novel resin technology.

Litho graphic Inks formulations
Conventional UV Lithographic inks require substantial quantities of mixed photoinitators to ensure optimum cure and develop proper adhesion in the printing process. These photoinitiators are typically low molecular weight compounds that can produce volatile or toxic byproducts after decomposition and may migrate into food package they can also be expensive, malodorous, and may contribute to film yellowing, which can limit their applicability, in general, an may render them unsuitable for use in while and light –colored inks. Functionalized oligomeric photoinitiators may overcome some of these drawbacks. However, multi-step synthesis may be required for their manufacture,
The amount of traditional photoinitiator in offset ink formulations can be significantly reduced by using the self initiating acrylate oligomer technology described in this paper.
In tables 1 to   UV offset ink formulations are given and performance properties are described.   The inks were made by grinding the formulations using three roll mills and quality of grind evaluated using NPIRI grind gauge.

Lithographic Ink Testing:

Tack: Tack is the measurement of frictional torque induced by drag forces in the splitting of an ink film. The electronic inkometer is a three roller distribution system designed to operate at speeds similar to an offset ink press
Methodology: Tack was measured according to ASTM D4361-89 using a Thwing-Albert Electronic Inkometer. A Pipet was filled with 1.32cc of ink. The ink was distributed on the rollers of the inkomter. The inkomter was turned on (1200RPM) and the tack values were recorded every thirty seconds for the first two minutes and then every minute to ten minutes. The one minute and final tack values are reported.

Duke Emulsification: The test is designed to predict the emulsification of ink. Inks that do not emulsify enough fountain solution have a tendency to scum on the press, similarly, inks that over emulsify provide poor print quality and excessive dot gain.
Methodology: Duke Emulsification testing was performed according to ASTM method D4942-89. Fifty grams of ink were placed in the mixing bowl. Twenty milliliters of fountain solution were added to the mixing bowl and mixed together at 90 RPM for one minute. Any fountain solution not absorbed by the ink was decanted and the mixing bowl was weighed. Twenty milliliters of fountain solution was added to the mixing bowl again and the test repeated. This was done 10 times. An Emulsification curve was generated from the data as well as final emulsification percentage. The pH and conductivity of the fountain solution before and after the test was also recorded

Table 1: Process Black Lithographic Ink

Raw Material	Weight %	Comments
Carbon Black	13	Mogul E Cabot Corp
Pigment Violet 23	1	Sun Chemical
Pigment Blue 15:4	2	Sun Chemical
DREWRAD 1123	35.5	Ashland Inc
DREWARD 1123 L	29.5	Ashland Inc
Propoxylated Glyceryl Triacrylate	10	Sartomer Inc
Talc	2	RTV Inc
Polymerization Inhibitor	1	Rahn AG
PI Blend	6	
Total	100	
Viscosity (Cone and Plate)	100 P	

Tack Values for Process Black Lithographic ink:

Time	Tack Value	Misting
30 sec	14	None
60 sec	14	None
90 sec	14.2	None
03 min	14.6	None
04 min	14.8	None
05 min	15.2	None
06 min	15.4	None
07 min	15.7	None
08 min	16.1	None
09 min	16.0	None
10 min	16.8	None

Duke Emulsification

Distilled Water pH 6.8 conductivity 33.5				
Sample	% Water Pick -up	Bleed	pH after	Conc. After
Process black	38	None	7.0	319
Fountain solution pH 3.6 Conductivity 2206				
Sample	% Water Pick -up	Bleed	pH after	Conc. After
Process black	29	None	550	2250

Table 2: Process Cyan

Raw Material	Weight %	Comments
Pigment Blue 15:4	15	Phthalate Blue
DREWRAD 1123	35.5	Ashland Inc
DREWRAD 1123 L	30.5	Ashland Inc
Propoxylated Glyceryl Triacrylate	11	Sartomer
Talc	2	RTV Inc
Polymerization Inhibitor	1	Rahn AG
PI Blend	5	
Total	100	
Viscosity (Cone and Plate)	90 P	

Tack Values for process cyan Lithographic ink

Time	Tack Value	Misting
30 sec	17.0	None
60 sec	17.1	None
90 sec	16.9	None
120 sec	17.4	None
03 min	17.4	None
04 min	17.9	None
05 min	17.9	None
06 min	17.9	None
07 min	18.1	None
08 min	18.2	None
09 min	18.4	None
10 min	18.5	None

Duke Emulsification

Distilled Water pH 6.8 conductivity 33.5				
Sample	% Water Pick -up	Bleed	pH after	Conc. After
Process Magenta	38	None	7.3	170
Fountain solution pH 3.6 Conductivity 2206				
Sample	% Water Pick -up	Bleed	pH after	Conc. After
Process Magenta	29	None	5.5	2500

Table 3: Process Magenta

Raw Material	Weight %	Comments
Pigment red 57:1 (Lithol Rubine)	14	Calcium Lithol
DREWARD 1123L	68	Ashland Inc
Propoxylated Glyceryl Triacrylate	10	Sartomer
Talc	2	RVT Inc
Polymerization Inhibitor	1	Rahn AG
Photoinitiator Blend	5	
Viscosity Cone and plate	75 P	

Tack Values for Process Magenta Lithographic ink:

Time	Tack Value	Misting
30 sec	14.8	None
60 sec	14.9	None
90 sec	15.4	None
120 sec	15.4	None
03 min	16.2	None
04 min	16.4	None
05 min	16.9	None
06 min	17.3	None
07 min	17.6	None
08 min	17.9	None
09 min	19.1	None
10 min	19.4	None

Duke Emulsification

Distilled Water pH 6.8 conductivity 33.5				
Sample	% Water Pick -up	Bleed	pH after	Conc After
Process Magenta	44	None	7.3	150.8
Fountain solution pH 3.6 Conductivity 2206				
Sample	% Water Pick -up	Bleed	pH after	Conc After
Process Magenta	35	None	5.5	2770

Table 4: Process Yellow

Raw Material	Weight %	Comments
Pigment Yellow 13	14	AAMX Yellow
DREWRAD 1123L	68	Ashland Inc
Propoxylated Glyceryl Triacryalte	10	Sartomer
Talc	2.0	RVT Inc
Polymerization Inhibitor	1.0	Rahn AG
Photoinitiator Blend	5.0	
Viscosity (Cone and Plate)	80 P	

Tack Values for Process Yellow Lithographic ink

Time	Tack Value	Misting
30 sec	21.4	None
60 sec	19.8	None
90 sec	18.6	None
3 min	17.9	None
4 min	16.7	None
5 min	16.7	None
6 min	16.6	None
7 min	16.7	None
8 min	16.7	None
9 min	16.9	None
10 min	17	None

Duke Emulsification

Distilled Water pH 6.8 conductivity 33.5				
Sample	% Water Pick -up	Bleed	pH after	Conc After
Process Yellow	35	None	7.75	966
Fountain solution pH 3.6 Conductivity 2206				
Sample	% Water Pick -up	Bleed	pH after	Conc After
Process Yellow	28	None	4.5	2380

Extractables testing of Novel radiation curable resins: The Novel self-initiating radiation curable resins described in the above formulations were tested for extractables using Reverse side extractables testing (Accelerated cell extraction method). The resins described above ink formulations were blended with Propoxylated glycerol triacrylate a widely used monomer that provides excellent ink-water interaction in UV curable Lithographic formulations. Draw downs were made on BOPP film and cured using one 300 watt/H bulb and cured and tested for extractables.

Overview of Analytical methodology: The samples were tested for UV-curable resin migrants in an extraction protocol using 95% ETOH as fatty food simulating solvent. The reverse side (food contact surface). of the substrate was exposed to extraction and analyzed for the presence of resin borne migrants.   The samples were screened for extractables using modified FDA conditions in an accelerated 24 hour incubation protocol.   The films were placed into extraction cells which were fabricated from 316 stainless steel and Teflon®. Each cell was then filled with 10 ml of 95% ethanol / 5% DI water. The cells were then heated at 40°C for 24 hours, after which they were removed from the oven, and then mechanically shaken for 1 hour. The cells were opened and the extract was poured into 8 dram vials. The extracts were concentrated to 2ml volume under dry nitrogen. One ml of the extract was transferred to a 1 dram vial. To enhance the quality of the analysis, each vial was spiked with ~48 ppb d-10 anthracene. A portion of this solution was transferred to an auto sampler vial for analysis by GC/MS. A 1μl aliquot was injected onto a 30-meter fused silica HP-FFAP capillary column attached to a mass selective detector. A solvent blank was run before each sample was analyzed to insure no carry over from any previous analysis. Each sample analysis was compared with a solvent blank and control extract analysis. Identification of analytes was achieved using the custom SEAFDA Library. Due to interference at retention time ~18.4 minutes the d-10 peak is not easily seen, but is noted in the attached TICs expanded views.

GC/MS (MSD-004)
Inj. Temp.   280°C
Det. Temp.   280°C
GC Temp. Program   35°C for 2 min. then 10°C/min. to 250°C for 10 min.
Split Ratio   5:1
Column   HP-FFAP (0.32 mm X 25 meters)
Injection   Autosampler 1 μl
Detection   Mass Selective Detector
Sample Prep   as described above

Results and Discussion

The sample extracts are being analyzed using GC/MS. The results from each analysis were compared to an ethanol blank and a control sample extract. The analysis of the blank and control extract are used for the identification of the extactables coming solely from the self-initiating resins used in ink formulations described above. The extracts of samples 1123 and 1123L both contained analytes are expected to be very low.

Conclusion:

A complete quantitative and qualitative analysis of all the migrants is underway and will be presented during the conference. The results are expected to lead to the conclusion that these materials, when used in the manner described, will meet the requirements to be generally regarded as safe (GRAS) when 95% ETOH food stimulant (fatty food stimulant) for individual components, which is a necessary condition for direct food contact applications. The best raw materials and starting point formulations showed very good performance in UV lithographic inks and data on extraction studies indicate that they are suitable for use in food contact applications and we highly recommend end user risk assessment.