CYTEC

Evaluation of Resins in Energy Curable Offset Inks

EBECRYL® Resins and ADDITOL® Additives for Graphic Arts

About Us

From defining more efficient processes for mining customers to developing new additives for polymer-based alternatives to wood and metals, the product lines of Cytec Specialty Chemicals are unified in their dedication to customer-driven innovation.

Working closely with our customers, we develop revolutionary technologies that enable them to improve performance and productivity, enter new markets, and refine new applications. How to improve mine profitability or coatings efficiency in the face of important environmental concerns? How to develop polymers that really stand up to UV light? How to use phosphines to create better, safer biocides and fumigants for agriculture? Our technology and sales teams work on-site with customers every day to address today's business challenges and troubleshoot tomorrow's.

The applications are diverse, but the commitment is uniform: finding better solutions for customers through continual research, ongoing collaboration and a passion for innovation.

An Expansive Portfolio

Cytec Specialty Chemicals is a complete solution provider for customers requiring high-value surface technologies in industries that include industrial coatings, automotive, architectural, wood and paper, graphics, adhesives and opto-electronics.

We offer out customers advanced and diverse products and technologies for surfaces with an emphasis on environmentally friendly products such as UV/EB curable resins and additives, powder coating resins and additives, as well as waterborne and solventborne liquid coating resins and additives.

We are committed to working with our customers to develop environmentally advanced solutions and we are dedicated to open communication concerning the safe handling, distribution, use and disposal of the products we make.

A Focus on Customer Satisfaction

Cytec Specialty Chemicals operates a globally integrated set of order fulfillment IT systems and processes. All Spec Chem personnel in the order fulfillment processes are dedicated to delivering customer satisfaction through reliable and cost-effective supply of products to our customers. Cytec Specialty Chemicals has specialized personnel in Customer Service, Procurement, Manufacturing, Planning and Logistics to achieve this goal. In addition to timely and accurate order fulfillment, there is an equally important focus on maintaining safety and protecting the environment at all steps in the process, from the procurement of raw materials to the delivery of finished goods to the customer's door.

Dedication to Operational Excellence

Cytec's Spec Chem Manufacturing Organization operates globally to provide superior service to our customers in all regions. Our vision of operational excellence brings value to our customers through on-going, continuous improvement initiatives, including Lean Manufacturing, Six Sigma Principles, and Best Practice Engineering. Our value proposition is driven by excellence in our Safety, Environmental, Quality Systems and Employee Development Programs. We are structured by business technology, which enables our sites to work transparently with R&D, Customer Service and the Business, to share best practices across common processes. We also are able to gain leverage from overall global manufacturing synergies to most efficiently meet customer needs.

Key Product Lines

- Liquid Coating Resins and Additives
- Mining Chemicals
- Phosphine and Phosphorus Specialties
- Polymer Additives
- Powder Coating Resins and Additives
- RADCURE® UV/EB
- Specialty Additives

Provider of Innovative Solutions to the Graphics Industry

We are committed to consolidating our leadership position as the preferred supplier to the global energy-curable graphics industry. We shall continue to deliver added value to our customers through innovative market-driven solutions based on technological and operational excellence.

To fulfill our objective of delivering superior value to our customers, we have a dedicated technical service team investigating inks and varnishes requirements for all printing processes. Based on this, we have designed a full range of UV/EB vehicles, binders and resins that address the most stringent needs of the energy-curing graphics market.

With numerous plants, research and technical service centers around the world, we are in a strong position to satisfy the multidimensional requirements of our customers with unrivalled world-class levels of service.

Table of Contents

General Principles of the Lithographic Process

Lithography is a planographic process, in that the ink-carrying image is in the same plane as the non-image areas. On the plate, areas of different surface energy are created by chemical treatment. This process leads to the formation of image areas that are ink accepting and water repellent, and non-image areas that are water accepting.

Usually, the plate is damped before it is inked. The fountain solution - consisting of water, buffer salts, surface active agents, and other additives and possibly isopropanol – forms a film on the non-image areas (water accepting), but contracts into tiny droplets on the image areas (water-repellent). *(See Fig.1).*

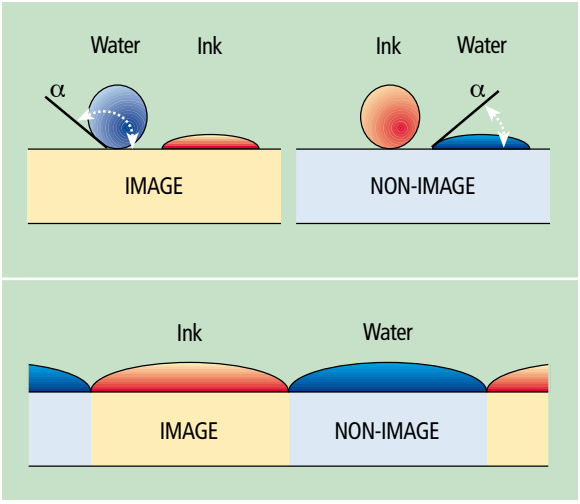


Fig. 1: Lithographic principle.

When an inked roller passes over the damped plate, the water film on the non-image areas prevents these being inked up and pushes the ink towards the image areas. The water droplets present on the image areas are either removed or emulsified into the ink. If the ink is too water repellent and this emulsification does not take place, an uneven "mottled" print will result. Emulsifcation of too much water in the ink may lead to a loss of transfer and hence a loss of optical density of the print.

A proper "water window" is necessary to be able to print with varying levels of fountain solution emulsified. It is important that when water is emulsified in the ink, the ink rheology undergoes a minor change. This is necessary to obtain a constant ink transfer and thus stable press behavior.

To print correctly in lithography, the right balance between ink and fountain solution must be achieved, thus comes the term "ink water balance".

2 Introduction to Energy Curable Offset

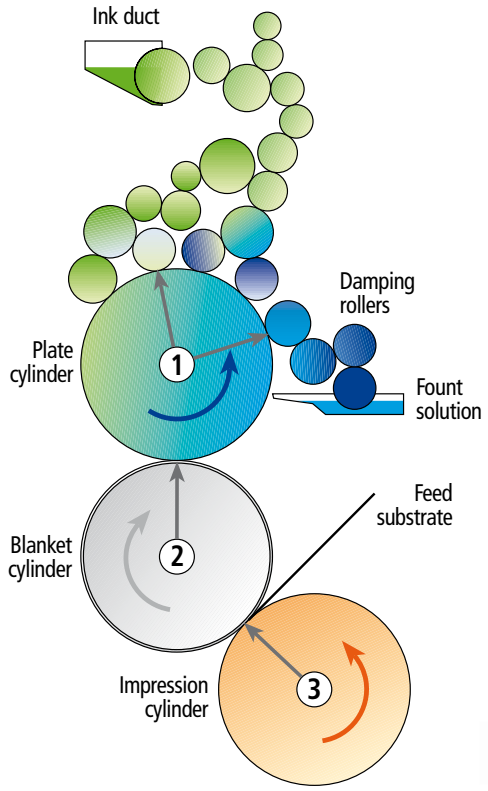
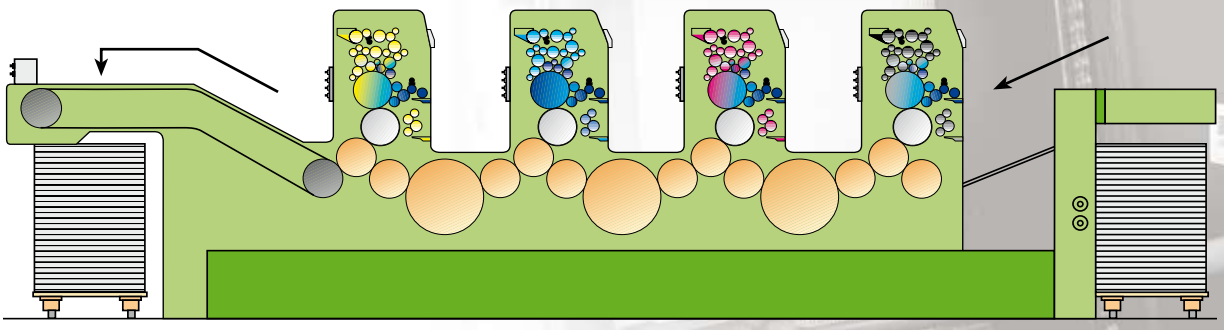


Fig. 2: Offset Lithographic Process.

The process is called offset lithography *(see Fig. 2)* because the ink is not transferred directly from the plate to the substrate, but is first "offset" onto a rubber blanket cylinder and is then transferred to the substrate.

The offset lithographic process dominates the graphic industry in a wide range of formats: from multiple color 8½" x 11" *(Sheet-fed printing, see Fig. 3)*, to printing magazines and newspapers on a continuous web of paper (web offset). This process is particularly suited to the production of lightweight packaging, books, magazines, newspapers, brochures, maps, promotional posters and literature, business stationery, to name some examples.

Fig. 3: Schematic presentation of a Sheet-fed Offset printing machine.



Types of Offset Lithographic Inks:

Offset lithographic inks are often characterised according their drying method:

- Absorption: cold-set inks (eg. newspaper inks)
- Evaporation: heat-set inks
- Oxidation: conventional sheet-fed inks
- Energy curing (UV/EB)

Energy Curable Offset inks are used in sheet-fed and web-fed applications. The setting and the drying of the ink occur in approximately 0,1 s. by transforming the wet binder into an insoluble dry ink film through a polymerisation reaction. The polymerisation is induced by UV light (or electron beam).

Energy curable inks mainly consist of:

- Acrylated resins (oligomers): basic coating properties
- Monomers (di- to hexa acrylates): viscosity reduction, flexibility (monofunctional); crosslinking (multifunctional
- Pigments and fillers
- Additives: performance fine tuning
- Photoinitiator package: free radical generation to initiate polymerisation

Typical Properties of Energy Curable Offset Inks:

- Immediate drying (surface and in-depth)
- On-line processing
- No spray powder needed in sheet-fed offset
- Increased productivity
- No solvents used
- No drying of ink on the printing press (less cleaning)
- Low energy level required (vs heat drying)
- Ability to print on a wide variety of substrates with the same ink
- Printing on heat-sensitive substrates
- Reduced space required (vs heat drying)
- High gloss
- High chemical resistance

Offset Ink Parameters and Test Methods

Ink Parameters

Inks used for the lithographic industry must fulfil a number of requirements:

- Suitable Viscosity (expressed in Pa.s or poise)
- Low tack (at 1200 RPM, 90° F)
- Low misting
- Good ink-water balance
- Good reactivity

During the last decades, a number of methods have been developed to evaluate properties of wet inks and printed (dried) inks. We have chosen the following laboratory methods to assess the above characteristics.

Lithographic Inks Evaluation Capabilities at Cytec Specialty Chemicals, Americas

Oligomer Viscosity

- Definition:
  Viscosity is defined as a fluid's resistance to flow. There are a number of available instruments and methods to measure viscosity.

- Equipment:
  - Brookfield Rotational Viscometer, Model RVDV
  - Brookfield Thermosel Chamber or Small Cell Adapter
  - Electronic Temperature controller or programmable circulating water bath
  - Brookfield Sample Container
  - Brookfield Spindles

- Material:
  - Oligomer sample

- Testing Method:
  - Appropriate oligomer sample size is added to Brookfield sample container
  - Select RPM and spindle number by selecting the appropriate button on the viscometer keypad
  - Measure and record viscosity

Tack

- Definition:
  Tack is a relative measurement of the cohesion or stickiness of an ink film. Tack is measured by measuring the force required to split an ink film between two rollers. The tackier the ink, the higher the force required for film separation. Tack is recorded in arbitrary units, depending on instrument used for measurement.

- Equipment:
  - Thwing-Albert Electronic Inkometer *(See Fig. 4)*

- Material:
  - 0.2 cc ink

- Testing Method:
  - Ink is applied to bottom vibrator roller and manually spread onto the other rollers
  - Initiate testing at 1200 RPM, 90° F
  - Ink tack is recorded after 1 minute

Fig. 4: Thwing-Albert Electronic Inkometer.

Lithographic Inks Evaluation Capabilities at Cytec Specialty Chemicals, Americas

Misting

- Definition:
  Ink misting is the fine mist or spray of ink thrown off rapidly moving rollers *(See Fig. 5)*.

- Equipment:
  - Thwing-Albert Electronic Inkometer
  - Spectrodensitometer

- Materials (ink misting is usually measured at the same time as ink tack):
  - 0.2 cc ink
  - Coated white paper (trimmed to fit into bottom inkometer tray)

- Testing Method:
  - A piece of coated white paper is placed in the tray beneath the bottom inkometer roller
  - Begin testing at 1200 RPM, 90° F, 1 min.
  - After completing the tack testing, the paper is removed and the ink area is divided into quadrants *(See Fig. 6)*
  - In each quadrant, the total color difference (ΔE) between unexposed paper and the test specimen is measured
  - The average of the four readings is reported.
    - Note: This is not an absolute value but indicates an ink's tendency to exhibit misting

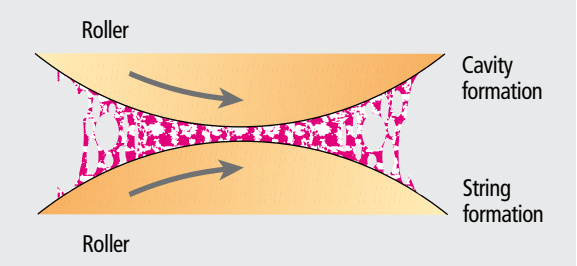


Fig. 5: Ink film splitting.

Fig. 6: Example of misting result.

Reactivity (Cure Speed)

- Definition:
  Reactivity is the speed or rate of polymerization of an energy curable ink. Technically, reactivity is the energy density required to dry, curing or polymerize the ink film. Reactivity is reported as energy density and expressed as J/cm^2 or mJ/cm^2.

- Equipment:
  - Aetek UV Curing System
    - 1-400 watts/in. UV lamp
  - Radiometer (light bug)
  - "Little Joe" Proofing System with wedge plate

- Materials:
  - Coated white paper
  - Ink

Lithographic Inks Evaluation Capabilities at Cytec Specialty Chemicals, Americas

- Testing Method:
  - Ink is applied to coated paper at appropriate film thickness using "Little Joe" proofer and exposed to curing source
  - After exposure, the ink surface is vigorously rubbed with the index finger
    - If no ink removed, the ink is cured at this exposure. Using a radiometer, the energy density is measured and recorded. Also recorded is the conveyor/belt speed
    - The conveyor/belt speed is increased the test is repeated until ink is removed
    - If in the initial testing, ink is rubbed off, the conveyor/belt speed is decreased and the test repeated until ink is not removed by rubbing the surface
    - The shortest exposure (lowest energy density) needed to achieve no ink removal is reported as the ink reactivity

Adhesion to Non Porous Substrates

- Definition:
  Adhesion is ability of an ink to bond completely with the substrate. When there is full adhesion the ink is not removed in standard tape testing. There are two methods used for tape test adhesion testing – tape pull on filmic substrates and cross hatch on rigid substrates. Adhesion is typically expressed as percent of ink adhering or remaining on the substrate.

- Equipment:
  - Aetek UV Curing System
    - 1-400 watts/in. UV lamp
  - "Little Joe" Proofing System with wedge plate
  - Specified test tape (usually 3M's 600 or 610 tape)
  - Cross hatch tool

- Materials:
  - Specified non-porous substrate
    - Coated
    - Uncoated
  - Ink

- Testing Method:
  - Ink is applied to substrate at appropriate film thickness using "Little Joe" proofer and then cured with appropriate energy density
  - After curing, a strip of test tape is applied to the ink surface
    - If testing adhesion to a rigid substrate, a cross hatch tool is used to score the ink film prior to applying the tape
  - At a 60° angle, the tape is quickly ripped from the ink surface
  - The percent ink remaining on the substrate is determined and reported

Printability

- Definition:
  Printability is the ink's behavior in a lithographic printing environment.
  This testing simulates the handling and application of an ink at a printer's facility.
  The testing evaluates ink transfer, ink-water balance, image quality and productivity.

- Equipment:
  - Ryobi CD 2800 Duplicator outfitted with integrated dampening system and UV curing system *(See Fig. 7)*

- Materials:
  - 70# coated paper
  - Fountain solution
  - Ink

- Testing Method:
  - Ink is printed in accordance with industry procedures
  - During printing, ink is evaluated for ease of establishing and maintaining color density and print contrast
  - Also evaluated are press make ready and clean up

Fig. 7: Ryobi CD 2800 Duplicator.

Products for Energy Curable Lithographic Inks

This section describes products recommended for energy curable offset inks. General recommendations are given on the use of the different types of acrylates in energy curable offset inks. Features and benefits of each product are also mentioned.

General Recommendations

Product Type	Benefits
Polyester acrylates	Pigment wetting Ink water balance
Diluted polyesters	Adhesion to plastics and metals
Epoxy acrylates	Reactivity Hardness; scratch resistance Solvent resistancy
Modified epoxy acrylates	Improved ink water balance
Urethane acrylates	Reactivity (dark colors) Hardness; scratch resistance Solvent resistancy
Diluting acrylates	Viscosity/tack adjustment

Polyester Acrylates

Products	Functionality, Theoretical	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL® 657	Tetrafunctional	103500	• Good pigment wetting, especially yellow pigments • Provides ink with higher ink tacks
EBECRYL 811	Trifunctional	90000	• Very low ink misting • Provides very good ink-water balance
EBECRYL 838	Hexafunctional	49298	• Good surface hardness • Good chemical resistance
EBECRYL 846	Tetrafunctional	45000	• Good reactivity • Suitable for paper and board on web presses
EBECRYL 870	Hexafunctional	43070	• Excellent pigment wetting • Good overall lithographic properties
EBECRYL 871	Hexafunctional	47450	• Excellent pigment wetting • Provides ink with lower ink tacks
EBECRYL 889	Tetrafunctional	32300	• Good adhesion to super-calendared paper • Good printability to super-calendared paper
EBECRYL 1657	Tetrafunctional	124800	• Purified version of EBECRYL 657 • Low residual odor

Diluted Polyesters

Products	Description	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL 436	Chlorinated polyester in 40% TMPTA	100000	• Good adhesion to non–porous substrates • Good adhesion to metals
EBECRYL 438	Chlorinated polyester in 40% OTA 480	85600	• Good adhesion to non–porous substrates • Good adhesion to metals
EBECRYL 586	Chlorinated polyester in 40% TMPTA	45029	• Good adhesion to non–porous substrates • Good flexibility

Products for Energy Curable Lithographic Inks *(continued)*

Epoxy Acrylates

Products	Description	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL 860	Epoxidized Soya Oil Tetra-Acrylate	26518	• Good flow and leveling • Good compatibility with hybrids inks
EBECRYL 3411	Fatty Acid Modified Epoxy Diacrylate	40100	• Good pigment wetting • Good flow and leveling
EBECRYL 3701	Modified Bisphenol A Epoxy Diacrylate	1600000	• High reactivity • Increases ink tack
EBECRYL 3702	Fatty Acid Modified Epoxy Diacrylate	495000	• Increased flexibility • Increases ink tack
EBECRYL 3708	Modified Bisphenol A Epoxy Acrylate	190000	• Provides flexibility • Recommended for metal deco
EBECRYL 3720	Bisphenol A Epoxy Diacrylate	750000	• Good solvent resistance • Increases ink tack

Urethane Acrylates (used as additives)

Products	Description	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL 220	Aromatic Urethane Hexacrylate	28268	• Enhances reactivity in dark colored inks • Enhances scratch resistance
EBECRYL 230	Aliphatic Urethane Diacrylate	44014	• Increases flexibility • Low Tg
EBECRYL 1290	Aliphatic Urethane Hexacrylate	85000	• Enhances hardness • Increases scratch resistance
EBECRYL 4827	Aromatic Urethane Diacrylate	238000	• Enhances flexibility • Enhances adhesion to plastics

Diluting Acrylates

Products	Description Theoretical	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL 1039	Urethane Monofunctional Acrylate	40	• Enhances adhesion to non-porous substrates • Good reactivity (for monofunctional monomer)
EBECRYL 113	Aliphatic Monofunctional acrylate	120	• Enhances adhesion to non-porous substrates • Good pigment wetting • Good reactivity (for monofunctional monomer)
TRPGDA	Tripropylene Glycol Diacrylate	12.9	• Good diluent • Good reactivity without brittleness
$NPG(PO)_2DA$	Neopentyl Glycol Propoxylate Diacrylate	15.9	• Increases flexibility • Lower surface tension
EBECRYL 150	Bisphenol A Ethoxylate Diacrylate	1347	• High reactivity • Enhances scratch resistance
TMPEOTA	Trimethylolpropane Ethoxy Triacrylate	21	• Good reactivity • Increased flexibility (vs. TMPTA)
OTA 480	Propoxylated Glycerol Triacrylate	88	• Good pigment wetting • Good reactivity
TMPTA	Trimethylolpropane Triacrylate	108	• Increases crosslinking and hardness • Good chemical resistance
EBECRYL 40	Polyether Tetra-acrylate	147	• Good reactivity • Good hardness without brittleness
EBECRYL 140	Di-trimethylolpropane Tetra-acrylate	979	• High crosslinking • Increased hardness
DPHA	Acrylated Dipentaerythriol	17093	• High reactivity • Increased hardness

Specialty: Bioligomers – Renewable

Products	Description	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL 5500	Glycerol Derivative Triacrylate	110	• Partially based on renewable resources • Good cure response • Hardness
EBECRYL 5610	Modified Epoxy Acrylate	2200	• Partially based on renewable resources • Developed for OPV's • Good flow and leveling
EBECRYL 5820	Polyester Tetra-Acrylate	66100	• Partially based on renewable resources • Good pigment wetting
EBECRYL 5821	Polyester Pentaacrylate	27500	• Partially based on renewable resources • Good reactivity
EBECRYL 5822	Polyester Pentaacrylate	29200	• Partially based on renewable resources • Good color development with carbon blacks

Products for Energy Curable Lithographic Inks *(continued)*

Specialty: Low Odor and Low Extractables

Products	Description	Viscosity, cP @ 25°C	Key Features and Benefits
EBECRYL LEO® 10501	Trifunctional Diluting Acrylate	80	• High reactivity • Lower viscosity
EBECRYL LEO 10601	Modified Epoxy Acrylate	200000	• Good solvent resistance • Good reactivity
EBECRYL LEO 10801	Hexafunctional Polyester Acrylate	48000	• Good pigment wetting • High reactivity

Additives

	Products	Type	Key Features and Benefits
Photoinitiators	ADDITOL® BCPK	Mixture	• Easily incorporated • Good combination of surface and through cure
	ADDITOL DX	Mixture	• Liquid photoinitiator • Effective in pigmented inks at 5-10% levels
	ADDITOL LX	Mixture	• Liquid photoinitiator • Effective in white and yellow inks at 5-10% levels
	ADDITOL BP	H-Abstraction	• Good solubility • Excellent surface cure
	ADDITOL BDK	α-cleavage	• Good solubility • Multipurpose photoinitiator – use alone or combined with other photoinitiators
	ADDITOL CPK	α-cleavage	• Good solubility • Good surface an through cure
	ADDITOL HDMAP	α-cleavage	• Liquid photoinitiator • Good solvency of solid photoinitiators
	ADDITOL ITX	H-Abstraction	• Good solubility • Good through cure
	ADDITOL TPO	α-cleavage	• Low yellowing in white pigmented inks • Good through cure
	EBECRYL P39	H-Abstraction	• Low residual odor • Pourable liquid
Miscellaneous	EBECRYL 350	Silicone Diacrylate	• COF reduction • Non-migratory
	EBECRYL 1360	Silicone Hexaacrylate	• COF reduction • Non-migratory • Especially effective in EB

General Properties of Products for Energy Curable Lithographic Inks *(Relative ranking)*

Products	Viscosity	Reactivity	Pigment Wetting	Ink Tack	Ink Misting	Printability	Adhesion to Non-porous Substrates
EBECRYL 113	N/A	●●●	●●●	N/A	N/A	N/A	●●●●
EBECRYL 1039	N/A	●●●	●●●	N/A	N/A	N/A	●●●●
EBECRYL 150	N/A	●●●	●●	N/A	N/A	N/A	●
OTA 480	N/A	●●●	●●●●●	N/A	N/A	N/A	●
EBECRYL 40	N/A	●●●●	●●●	N/A	N/A	N/A	●
EBECRYL 140	N/A	●●●●	●●●	N/A	N/A	N/A	●
DPHA	N/A	●●●●●	N/A	N/A	N/A	N/A	●
EBECRYL 436	●●	●●	●	●●●	●●●	N/A	●●●●●
EBECRYL 438	●●	●●	●	●●●	●●●	N/A	●●●●●
EBECRYL 586	●●	●●	●	●●●	●●●	N/A	●●●●●
EBECRYL 657	●●	●●●●●	●●●●●	●●●	●●●●	●●●●●	●●
EBECRYL 811	●●	●●●	●●●	●●●●	●●●●●	●●●●●	●●●
EBECRYL 838	●●●●●	●●●●●	●●●●	●●●	●●●	●●●●	●
EBECRYL 846	●●●●●	●●●●●	●●●●	●●●●	●●●●	●●●●	●
EBECRYL 860	●●●	●●●	●●	●●●	●●	●●	●●
EBECRYL 870	●●●●●	●●●●●	●●●●●	●●●●	●●●●	●●●●●	●●
EBECRYL 871	●●●●●	●●●●●	●●●●●	●●●●	●●●●	●●●●●	●
EBECRYL 889	●●●●	●●●●	●●●●	●●●●	●●●●	●●●●	●
EBECRYL 1657	●●	●●●●●	●●●●●	●●●●	●●●●	●●●●	●
EBECRYL 3411	●●●●	●●●	●●●●●	●●●	●●●	●●●	●
EBECRYL 3701	●	●●●	●●	●	●●●	●●	●
EBECRYL 3702	●	●●●	●●●	●	●●●	●●	●
EBECRYL 3720	●	●●●	●●	●	●●●	●●	●
EBECRYL 220	N/A	●●●●●	N/A	N/A	N/A	N/A	●
EBECRYL 230	N/A	●●●	N/A	N/A	N/A	N/A	●●●
EBECRYL 1290	N/A	●●●●●	N/A	N/A	N/A	N/A	●
EBECRYL 4827	N/A	●●●	N/A	N/A	N/A	N/A	●●●

N/A = Not Applicable

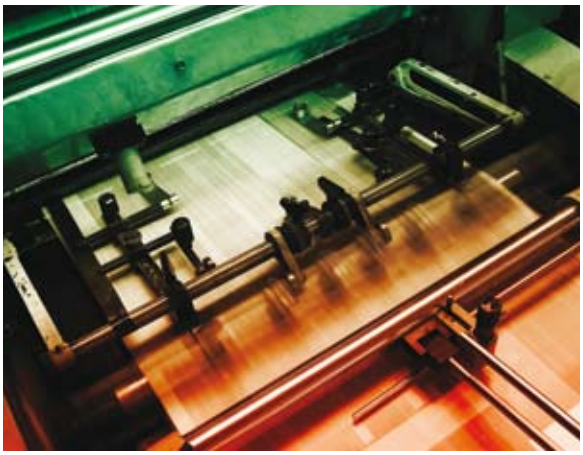
Key	● → ●●●●●	
Adhesion to Non-Porous Substrates	Poor	Excellent
Ink Misting	High	Low
Ink Tack	High	Low
Pigment Wetting	Poor	Excellent
Printability	Poor	Excellent
Reactivity	Low	High
Viscosity	Higher	Lower

Standard Ink Formulations for Evaluation of Oligomers for Energy Curable Lithographic Inks

The formulations indicated below have only been designed to provide us with a test method to evaluate our new development products. They are representative enough to give an indication of the way our products perform in Energy Curable Offset Inks. However, they can not be considered as recommanded formulations and are not meant to deliver optimal performance in all applications.

Paper and Board Stock:	
Pigment Dispersion	
Acrylated oligomer	50-60%
Polyester acrylate and/or epoxy acrylate	
Pigment	30-40%
OTA 480	5-10%
Ink	
Pigment dispersion	55-60%
Acrylated oligomer	20-30%
Polyester acrylate and/or epoxy acrylate	
Inert Filler	2-5%
Wax	0-2%
Diluting acrylate	2-5%
TRPGDA, TMPTA or TMPEOTA	
Additol DX liquid photoinitiator blend	8-10%

Non-Porous Stock:	
Pigment Dispersion	
Acrylated oligomer	50-60%
Diluted polyester	
Pigment	30-40%
OTA 480	5-10%
Ink	
Pigment dispersion	55-60%
Acrylated oligomer	20-30%
Diluted polyester acrylate	
Inert Filler	2-5%
Wax	0-2%
Diluting acrylate	2-5%
TRPGDA, NPG(PO)2DA, EBECRYL 1039 or EBECRYL 113	
Additol DX liquid photoinitiator blend	8-10%



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RAD-0004-A-EN-NA-12A

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