Urethane Acrylates – Additives for Energy Curable Lithographic Inks

Rosalyn Waldo
Surface Specialties UCB

Abstract:

Epoxy and polyester acrylates are typically used as backbones for energy curable lithographic inks. These oligomers provide the basic ink properties such as color development, misting tendencies and printability. To modify or improve ink performance urethane acrylates can be utilized. Ink properties such as flexibility, surface hardness and reactivity can all be enhanced with the addition of an appropriate urethane acrylate.
This poster reviews the use of urethane acrylates as additives for energy curable lithographic inks.

Introduction

Energy curable lithographic inks based on polyester acrylates have great utility and versatility. In addition to outstanding lithographic properties such as lower misting, adjustable ink tack and exceptional ink-water balance, these inks also exhibit good color development and good press runnability. At times it is necessary or desirable to enhance the performance of the polyester acrylate ink, to improve the adhesion to non-porous substrates, to improve flexibility or to increase the hardness of the ink film. Historically urethane acrylates have been used as additives to energy curable litho inks to achieve these enhancements. This is largely due to the availability of urethane acrylates with a wide range of physical properties such as functionality, tensile strength, glass transition temperature, and elongation.

In this study, several aliphatic and aromatic urethanes were evaluated for their effectiveness in modifying adhesion, flexibility, and hardness. These urethane acrylates are listed in Table 1, and have a variety of physical properties. The "softer" urethane acrylates were used to modify flexibility and adhesion while the "harder" ones were used to improve surface hardness. None of the test additives significantly altered lithographic properties.

Table 1: Physical properties – Urethane Acrylate Additives

Description		Tg, C	Tensile Strength, psi	Elongation,
Aromatic	Hard	49	8000	3
Aliphatic Diacrylate	Soft	-55	150	83
Aliphatic	Hard	--	6700	2
Aromatic Diacrylate	Soft	-6	900	900
Aromatic Triacrylate	Hard	82	8700	4
Aliphatic Diacrylate	Soft	--	--	--

Experimental

Two series of cyan inks were prepared. Both series began with the same 30% pigment dispersion, but used different oligomers or oligomer blends in the letdown. In the first series, a blend of polyester and urethane acrylates made up the oligomer portion of the letdown. Only the urethane acrylate was used as the oligomer in the letdown in the second series of inks. The complete formulae for both ink series are given in Table 2. Following preparation, the inks were applied to the test substrates at 0.20-.25 mil using a Little Joe proofer. The inks were cured using an RPC Aetek curing unit with one 400 watts/inch lamp.

Table 2: Formulae- Pigment dispersions and inks

Pigment Dispersion

Polyester acrylate	60%
OTA 480	10%
Irgalite blue, LGLD	30%

Inks – series #1

Irgalite blue, LGLD pigment dispersion	60%
Polyester acrylate	10%
Urethane acrylate	10%
OTA 480	5%
Inert filler	4%
Wax	1%
Photoinitiator blend	10%

Inks – series #2

Irgalite blue, LGLD pigment dispersion	60%
Urethane acrylate	20%
OTA 480	5%
Inert filler	4%
Wax	1%
Photoinitiator blend	10%

Results

Adhesion

Adhesion to non-porous substrates was measured using the Adhesion Tape test, ASTM # D 3359, method B. The ink films were scored using the cross hatch tool and the peel test performed with 3M 600 tape. The results were classified and reported in Table 3.

Table 3: Adhesion

% Adhesion to	PET-G	PC	Lexan	PS	RV	PVC
Polyester acrylate ink (control)	0	0	0	95	80	0
Series #1: Polyester and urethane acrylates in						
10% Aromatic urethane	0	0	0	100	35	0
10% Aliphatic urethane	0	0	0	25	85	0
10% Aliphatic urethane	0	0	0	100	65	100
Series #2: Urethane acrylate only in letdown						
20% Aromatic urethane	0	0	0	100	10	0
20% Aliphatic urethane	0	0	0	5	1	0
20% Aliphatic urethane	95	100	0	100	100	100

Legend:

PET-G: glycol modified polyethyleneterephthalate
PC: Polycarbonate
Lexan: Polycarbonate from General Electric
PS: Polystyrene
RV: Rigid vinyl
PVC: Polyvinyl chloride

At the 10% level, none of the urethane diacrylates were effective in improving adhesion to PET-G, polycarbonate, lexan polycarbonate, or rigid vinyl. The aliphatic urethane diacrylate B showed major improvements in adhering to the polyvinyl chloride. Similar results were seen with the urethane acrylates in series #2. Inks modified with the aliphatic or aromatic urethane diacrylates continued to show poor adhesion to the various plastics, while inks containing 20% of the aliphatic urethane diacrylate B exhibited 95-100% adhesion to most of the test substrates including PET-G and PC. Lexan was the one exception; none of the modified inks had good adhesion to this particular substrate.

Flexibility

To evaluate flexibility, the inks were modified with “softer” urethane acrylates, aromatic or aliphatic diacrylates. 2 ⅝ by 1 inch strips of coated substrate were bent 180° and examined for cracking and flaking along the crease. The comments in Table 4 indicate whether or not the ink film cracked. If there was flaking or loss of adhesion along the crease, the amount as a percentage of the length of the crack is listed in Table 5.

Table 4: Flexibility – Cracking

	PET-G	PC	Lexan	PS	RV	PVC
Polyester Acrylate control	Yes	Yes	Yes	None	Yes	Yes
Series #1: Polyester and urethane acrylate in letdown						
10% Aromatic urethane	Yes	Yes	Yes	None	None	Yes
10% Aliphatic urethane	Yes	Yes	Yes	None	None	Yes
10% Aliphatic urethane	Yes	None	Yes	None	Yes	None
Series #2: Urethane acrylate only in the letdown						
20% Aromatic urethane	None	None	None	None	None	None
20% Aliphatic urethane	Yes	Yes	Yes	None	Yes	Yes
20% Aliphatic urethane	Yes	None	None	None	None	None

Table 5 Flexibility – Flaking (loss of adhesion)

Percent of flaking	PET-G	PC	Lexan	PS	RV	PVC
Polyester Acrylate control	>90	>90	>90	0	25	20
Series #1: Polyester and urethane acrylates in the letdown						
10% Aromatic urethane	17	>90	49	0	0	0
10% Aliphatic urethane	0	21	>90	0	0	5
10% Aliphatic urethane	19	0	19	0	5	0
Series #2: Urethane acrylate only in letdown						
20% Aromatic urethane	0	0	0	0	0	0
20% Aliphatic urethane	13	19	19	0	0	29
20% Aliphatic urethane	19	0	0	0	0	0

The control polyester acrylate ink had cracking on all of the substrates except polystyrene and had extensive flaking on PET-G, PC and lexan. Inks modified with 10% aliphatic and aromatic urethane acrylates tended to have less cracking on rigid vinyl. 10% of the aliphatic urethane diacrylate B reduced cracking on polycarbonate and polyvinyl chloride. Flaking along the crease was a major problem with the control ink, but was significantly reduced with the experimental inks at both additive levels. The second series of inks, with 20% of the urethane additive in the letdown, exhibited far less cracking on all of the substrates. This was particularly true with the aliphatic urethane diacrylate B and aromatic urethanes. Interestingly, in many cases the modified inks that exhibited poor tape pull performance exhibited good flexibility and no loss of adhesion during the flexibility testing.

Surface Hardness

The softer, more pliable nature of polyester acrylate inks typically helps with adhesion to various substrates. Unfortunately, these softer films are also easy to scratch or mar. To improve ink film hardness and resiliency, an aliphatic and aromatic triacrylate were tested. The relative surface hardness of the ink film was measured using a nickel double rub procedure. The edge of a nickel was repeatedly rubbed against the ink film until the film either ruptured or fractured. The number of double rubs or strokes required to break through the film was recorded. The average of three readings is reported in Table 6.

Table 6: Surface Hardness (nickel double rubs)

	PET-	PC	Lexan	PS	RV	PVC	Coated Paper
Polyester acrylate,	5	1	2	14	4	7	8
Series #1: Polyester and urethane acrylates in							
10% aromatic	100	7	2	23	7	93	14
10% aliphatic	100	2	100	100	92	100	100
Series #2: Urethane acrylate only in the letdown							
20% aromatic	100	100	100	100	100	100	100
20% aliphatic	100	2	100	100	100	100	100

At the lower additive level the aliphatic urethane triacrylate was the most effective in increasing film hardness on the majority of the substrates. Whether at 10 or 20%, this urethane failed to improve the hardness of the film when printed on PC. The aromatic triacrylate was most effective at the higher level, achieving over 100 double rubs on all of the substrates.

Conclusion

As the results of this study indicate, urethane acrylates – aliphatic, aromatic, di or trifunctional can be used to drastically change the performance of polyester acrylate inks. Diacrylates can improve the flexibility of the ink as well as enhance adhesion to various substrates. The triacrylates will harden the film, improving its resistance to scratching, rubbing and marring.
As with other additives, diligence is required to successfully formulate with urethane acrylates. The formulator must consider a number of factors such as the influence of the substrate on performance, the "must-have" or critical performance criteria and the impact of that performance on the overall ink performance. Flexibility and hardness are opposing attributes as can be hardness and adhesion. Properly selecting the type and amount of an urethane acrylate to use can be instrumental in developing the best performing ink.

Acknowledgment

The author thanks Melissa Hedstrom for her technical assistance.