Evaluation of New Oligomers for UV/EB Lithographic Inks

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Abstract

UV/EB litho inks continue to show growth and added utility in the printing ink marketplace. Improvements in printing equipment technology have now placed more demands on the liquid ink printability and the cured ink properties. Although the oligomers currently used in these inks have very good printing properties, there are deficiencies that need to be addressed. In this project, the printability and cured ink properties of new acrylate oligomer backbones will be evaluated and compared to current technology.

Introduction

The lithographic printing process is more demanding than other printing processes on the oligomers, monomers, pigments, and additives, used in the formulations. Not only does an ink need to have the correct rheology and color strength, it must also transfer and emulsify properly during the process. Current oligomer chemistry has worked very well, but as printing presses become more advanced an evolution of the chemistry needs to follow. The following study was performed to evaluate next generation oligomers for their lithographic printing properties.

Experimental

A study was undertaken to understand the key lithographic printing properties that an oligomer used in ink formulations needs to have. Seven different oligomers with different backbones, but all designed to be used in litho inks, were part of the study. Four of the seven oligomers were experimental ones specifically designed for evaluation in this study. The other three are commercial oligomers that Sartomer currently sell in these types on inks. Comparison of the commercial and experimental oligomer provides a good benchmark for performance of the experimental ones and provides a useful comparison that ink formulators are familiar with.

Sartomer Designation	Paper Designation	Oligomer Description	Viscosity	Maximum Color
CN293	PEAc1	Acrylated Polyester Oligomer	7700 cps 25 °C	6G
CN294E	PEAc2	Acrylated Polyester Oligomer	4000 cps 60 °C	16G
CN2203	PEAc3	Polyester Acrylate Oligomer	1800 cps 60 °C	1G
PRO12119	AO1	Acrylate Oligomer	1800 cps 60 °C	1G
PRO11639	AO2	Acrylate Oligomer	4500 cps 60 °C	1G
NTX11777[1]	AO3	Acrylate Oligomer	4500 cps 60 °C	10G
NTX11817[1]	AO4	Acrylate Oligomer	5100 cps 60 °C	10G

Table 1. Oligomers evaluated in this study and their descriptions. [1] indicates that the oligomers were not on the TSCA inventory at the time of this paper's writing.

PEAc1, PEAc2, and PEAc3 are all commercial oligomers that have a successful history of performance in UV/EB lithographic ink formulations. The oligomers primarily are used to disperse pigment and impart desired rheology to the inks. The four new oligomers evaluated were designed to disperse pigments and to offer improvements in the rheology and properties of the cured ink films. AO1 and AO2 were originally designed for coatings formulations that needed improved heat resistance and dimensional stability after cure. The backbone is unique and provides the different properties seen from the oligomers. AO3 and AO4 utilize currently known backbones that perform well in ink formulations. To evaluate the properties of the different oligomers, UV lithographic inks were made and evaluated.

Component	%	Purpose or Structure
Oligomer	45.0	Component to be evaluated
Cabot Mogul E® Black	20.0	Black Pigment
SR492	15.0	Propoxylated Trimethylolpropane Triacrylate (PO TMPTA)
CD563	6.0	Alkoxylated Hexanediol Diacrylate
Ciba® Irgacure® 369	3.5	2-Benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone
Lamberti Esacure® KS300	3.0	Alpha-hydroxycyclohexyl-phenyl ketone
Lamberti Esacure® TZT	1.0	Blend of Methylbenzophenone and Trimethylbenzophenone
Lamberti Esacure® ITX	0.5	Isopropylthioxanthone
Rockwood Additives Claytone® HY	4.0	Clay
Byk® Cerflour® 991	2.0	Polyethylene Wax

Table 2. Black UV litho ink formulations.

Forty five percent of the various oligomers were incorporated into the formulation and evaluated. CD563 (alkoxylated HDDA) was used to lower the viscosity while minimizing the amount of monomer needed in the formulations. To increase the cure speed and cross link density SR492 (PO TMPTA) was used. . The photoinitiator package consisted of a blend of four components designed to cure pigmented ink with a medium pressure Hg arc lamp commonly found on printing presses. Claytone® HY was used in the final ink evaluations to modify the rheology of the inks. Ceraflour® 991 was utilized to provide surface properties, including slip.

The first, and probably most important, evaluation of the oligomers was the water balance. Understanding the water balance of the oligomers is key to any development effort. There are several ways to evaluate this property. Traditionally the Duke Emulsifier was the preferred laboratory test for understanding the water balance of a given ink. The method is still valid, but needs to be coupled with a higher speed emulsification test to gain the full picture of an ink's performance. The Duke is a low shear method that simply mixes the ink and fountain solution together. The amount of non-absorbed fountain solution is measured for each 100 cycles. For direct comparison sake, all of the water balance testing performed in this study was with 1.8% Fujifilm MXEH in water.

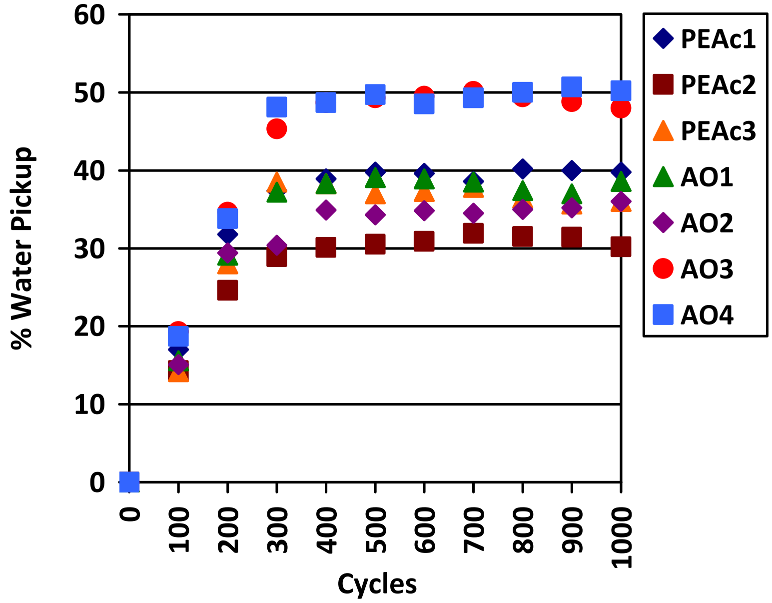

Chart 1. Water pickup versus cycles for Duke water pickup

Most commercial UV/EB lithographic inks have a water pickup between 30 and 50%, depending on the rheology of the ink and the desired fountain solution. Five of the inks had water pickups of less than 40%, indicating a good level of hydrophobicity in the oligomers. With this test the AO3 and AO4-based inks showed higher water pickup, but this is only half of the story.

The performance of litho inks in high shear emulsification testing is a better indicator of the performance of an ink on press. A Lithotronic (Novomatics Gmbh) utilizes an impeller to apply controlled shear to an ink. While under shear and constant temperature, fountain solution is added in increments. The equipment measures the torque on the impeller.

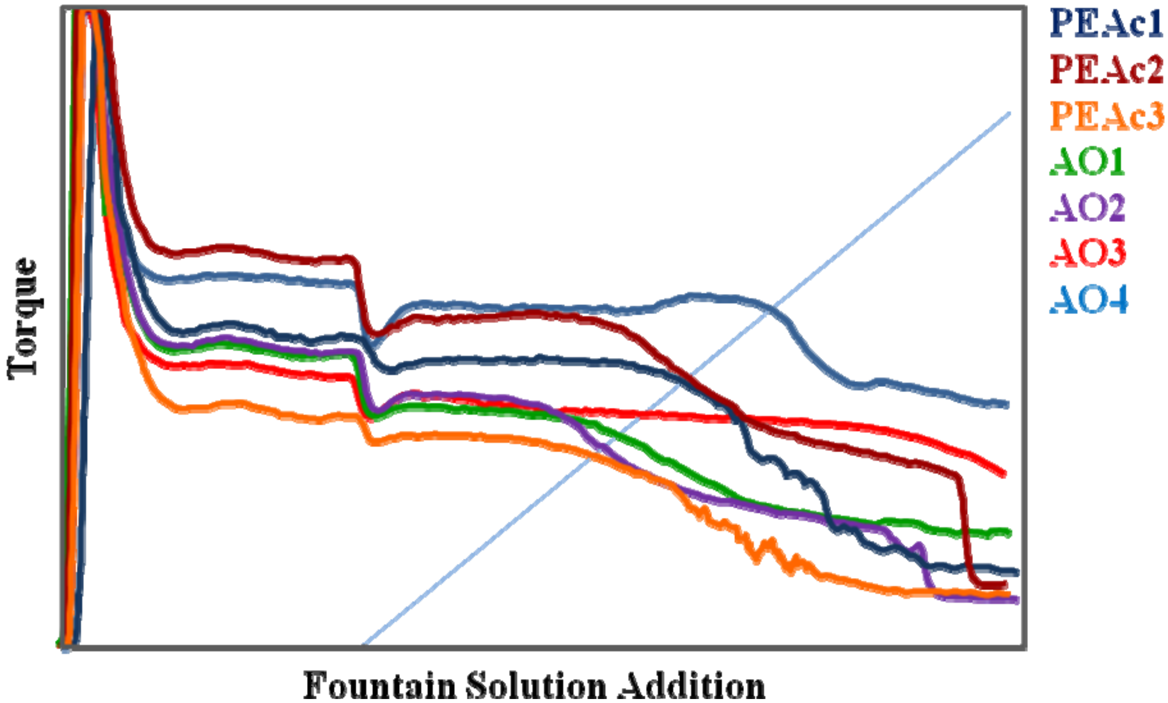

Chart 2. Lithotronic graph of fountain solution addition versus torque for the seven inks.

All of the seven different inks give varying results on the Lithotronic. The first two commercial oligomers, PEAc1 and PEAc2, show a good plateau in the torque after the fountain solution is added. The most desirable inks have a wide plateau in the torque that covers a wide amount of solution addition. This indicates that the ink's rheology is minimally changing as more fount is added and the ink emulsifies. PEAc3 ink shows a fairly short plateau, indicating that it is sensitive to high amounts of fount addition. The AO1 and AO2 inks have good torque plateaus, which when combined with the good water pickup values indicate that both oligomers have good water balance. The AO3 and AO4 inks have very unique Lithotronic profiles. Both inks do not change their rheology over a very wide range of fountain solution addition. Their ability to retain rheology is well beyond the other inks that were evaluated in this study. The AO3 and AO4 inks are a good example of why you combine different water balance tests. In the low shear testing they had water pickups on the higher end, whereas they exhibit excellent performance in high shear testing.

Another test that is useful in examining the water balance of oligomers in UV/EB litho inks is with a Tackoscope (Testprint BV). The Tackoscope is normally used to measure the dry tack of inks. The equipment, however, does have the ability to emulsify inks on a brass roller by the addition of a fourth roller to deliver fountain solution. In the test the inks equilibrate then are emulsified for 120 seconds. The recoveries of the inks are then examined to give an idea of performance.

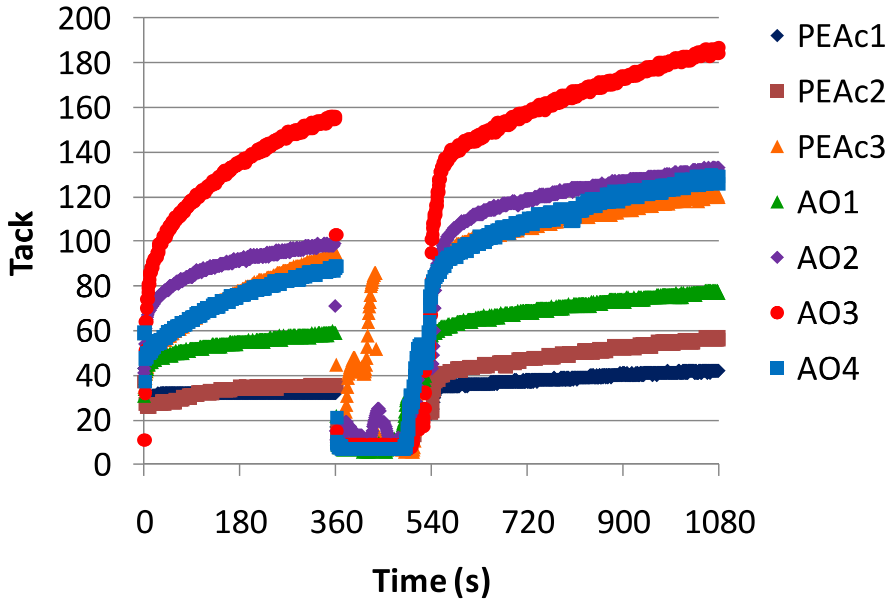

Chart 3. Tack versus time plots from Tackoscope testing.

There are several pieces of information that can be derived from the Tackoscope testing. The first piece is how quickly an ink will emulsify and will reach a stable, lower tack. In the graphs it can be seen in all of the inks, except for those based on PEAc3 and AO2, emulsify then maintain their stability. The PEAc3 and AO2-based inks did not immediately emulsify, indicating that they may be too hydrophobic. The second piece of data that can be derived is the quickness of tack recovery after emulsification. Once the emulsification roll is removed at 540 seconds, the inks start to recover their tack. Ideally the inks would very quickly recover tack and then plateau out. Although difficult to see on this graph, all of the inks except for AO4 show a very quick recovery. AO4 does start to recover quickly, but then has a brief period where the tack stabilizes.

The third piece of information can be found in the plateau after the inks have gone through initial recovery. The desired performance is to have a fairly flat plateau whose final tack value at 1080 seconds is ± 20% of the tack value at 360 seconds. Too much of a difference between the tacks can be an indication of issues with the ink. If the recovery tack is too high then the possibility exists that the inks were affected by the fountain solution of the emulsification process. Monomer loss to the fountain solution is a possibility. If the final tack is too low then the inks were too hydrophilic and over emulsified and were never able to recover the original tack. None of the inks tested in this study were over emulsified so they all had recovery tacks greater than their tacks at 360 seconds. The percent difference in tack at 360 seconds versus 1080 seconds is summarized in the table below. The AO3-based ink had the highest tack throughout the testing, but only showed an increase of 19.9% after emulsification. The PEAc2-based ink showed a dramatic tack increase of 55.6%.

Oligomer Ink	% Tack Change
PEAc1	31.8
PEAc2	55.6
PEAc3	28.7
AO1	30.5
AO2	33.3
AO3	19.9
AO4	46.6

Table 3. Tack differences between 360 seconds and 1080 seconds on the Tackoscope.

When the data from all three of the water balance tests are put together you get a clear picture of what the expected behavior of each oligomer is in a UV/EB lithographic ink. Comparing the four AO-based inks to the commercially utilized three PEAc's gives a good idea of water balance performance. AO1 and AO2 based inks showed low water pickups and similar emulsification tack recovery to the PEAc-based inks. In Lithotronic testing they do seem to have a narrower fountain solution addition range than the oligomers that were tested. AO3 and AO4-based inks exhibited an interesting combination of water balance properties. Both inks had Duke water pickups that were on the higher end of the desired range. However, when testing these same inks at higher shear rates they showed good performance. In Lithotronic testing both of the inks exhibited much more stable and longer torque values as more fountain solution was added. This indicates that the oligomers are able to be run at varying press speeds and fount additions without worrying about over-emulsifying the ink. The AO3 ink exhibited much better tack recovery in Tackoscope testing, whereas the AO4 ink saw a very dramatic increase in the final tack. From a water balance perspective, the AO3 oligomer seems to be the better oligomer for litho ink formulations.

Aside from the water balance, the seven different oligomers were also evaluated for standard litho ink testing including tack, rheology, cure speed and cleanup. Rheology can be broken down into two areas of interest, tack and viscosity. Tack, simply the measure of the energy needed to separate an ink film from itself, was measured on the Inkometer (Kershaw Instrumentation). The Inkometer is the standard instrument in the US ink industry for measuring the tack. Typically the tack is run at 400, 800, and 1200 rpm with the misting of the ink evaluated at the 1200 rpm speed.

Oligomer Ink	Tack 400 rpm	Tack 800 rpm	Tack 1200 rpm	Misting
PEAc1	1.1	2.8	4.2	Medium
PEAc2	1.4	3.1	4.5	High
PEAc3	3.0	6.0	8.1	Low
AO1	4.4	8.2	11.3	Low
AO2	5.3	9.9	13.3	Medium
AO3	8.8	12.4	16.4	Low
AO4	4.2	8.1	11.5	Medium

Table 4. Summary of tack readings of the seven inks.

The inks were designed so that the highest viscosity ink, AO3, had a tack of about 16 at 1200 rpm. The oligomer content was kept at the same level in the other inks, which explains the wide variance in viscosity of the inks. The PEAc1, PEAc2, and PEAc3 inks are much lower in viscosity than the newer oligomers, and that can been seen in the tack. The three PEAc inks are based on oligomers that are designed to wet pigment and have excellent flow in doing so. The higher amount of flow in the inks leads to misting on the Inkometer or on a commercial press. To reduce the misting some amount of elasticity needs to be introduced to the ink. This can be done by using a high amount of additives, such as clay and talc, in the inks or by increasing the elasticity of the liquid oligomers themselves. AO3 and AO4 were specifically designed to introduce some elasticity to the inks, while not introducing a high amount of thixotropic behavior. The misting of the AO3 and AO4 inks was reduced versus the other oligomers used in this study. Even though the AO1 and AO2 were not designed to have elasticity, they did impart lower misting to the litho inks.

While the inks were on the Inkometer they were examined for their cleanup-ability. In the last couple of years there has been a movement to run UV/EB litho inks on presses equipped with non-UV rollers and blankets. Printers desire to clean up the acrylate-based inks with their press wash designed for oil-based inks. Most acrylate-based inks will not easily clean up with these types of press washes. The seven inks were cleaned up using Prisco Autowash 6500.

Oligomer Ink	Cleanup-ability
PEAc1	Easy
PEAc2	Easy
PEAc3	Difficult
AO1	Medium
AO2	Medium
AO3	Easy
AO4	Easy

Table 5. The cleanup-ability of the seven inks based on the different oligomers.

The only ink that was very difficult to clean up with the 6500 was the one based on PEAc3. The other oligomers cleaned up easily with the 6500, with the AO3 and AO4 inks cleaning up the easiest.

To judge cure speed, the seven UV litho inks were printed with a Little Joe proofing press onto Lenetta charts and cured with a Fusion F600 “H” lamp (Fusion UV Systems, Inc.). The cure speed of the inks was judged by both the thumb twist for depth of cure and Q-tips for surface cure. The cure speed information in the table represents the failure of either the surface or deep cure of the inks.

Oligomer Ink	Cure Speed (fpm)	Cure Energy (mJ/cm^2)
PEAc1	500	86
PEAc2	500	86
PEAc3	650	66
AO1	800	54
AO2	675	64
AO3	600	72
AO4	800	54

Table 6. Cure speed measurements of the seven inks. The cure energy was measured by an EIT Power Puck® II.

All of the inks cured with very little energy and were generally in the same range for cure speeds. The AO1 and AO4 inks did exhibit exceptionally fast cure speed. In AO1 this is expected as the backbone is of a higher T_g and lower molecular weight than the other oligomers evaluated.

Conclusion

In this study the AO1, AO2, AO3, and AO4 oligomers exhibited the additional performance that new generations of oligomers can impart to UV/EB litho ink formulations. Newer techniques for evaluating water balance showed that the new oligomers had a wide window of emulsion stability that would translate well into press performance. The improved water balance, along with the proper rheology and curing properties, make these four oligomers good basis for the next generation of UV/EB litho ink formulations.