

New Polyester Polyols for Energy-Curable Ink Applications

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Pigment dispersion resins for energy-curable inks require excellent properties for pigment wetting, pigment dispersability and high pigment loading. In this study, two new polyols were developed, acrylated and evaluated in energy-curable ink applications. These polyols have low viscosity, handling ease and biorenewable content. Pigment dispersions and inks were prepared and evaluated for surface tension, pigment wetting, curability and rheological properties. The dispersions and inks made from the new resins had better rheological properties, pigment dispersion characteristics and higher

pigment loading properties compared to standard commercial resins that are typically used in energy-curable ink applications.

Energy-curing technology has been commercially available for more than 30 years and continues to gain acceptance as a technology for applications of coatings, inks and adhesives.¹⁻⁴ One of the main advantages of this technology is its extremely fast cure speed which results in higher production rates. Another advantage is the reduction in volatile organic compounds (VOCs).

In this investigation, two new polyol products were developed based

TABLE 1

Polyol characterization

Polyol	Hydroxyl Value (mg KOH/g)	Calculated Functionality (eq. OH/mol)	Viscosity @ 25°C (mPa·s)
STEPANPOL® PC-270-01	270	2.4	1,700
Agent 4087-25 (experimental)	328	3.6	16,860

TABLE 2

Characterization of polyester acrylates

Polyester Acrylate	Calculated Functionality (eq. acrylate/mol)	Viscosity @ 25°C (mPa·s)	Surface Tension (dynes/cm)
Acrylate A	2.4	491	35.8
Acrylate B	3.6	4,140	31.6
Control I	6	9,448	36.4
Control II	6	7,078	35.9

TABLE 3

Black ink dispersion formulations (weight percentages are shown)

Material	20% Pigment	30% Pigment	35% Pigment	40% Pigment
Oligomer	38.87	33.76	31.20	28.65
Tetrafunctional polyester acrylate	9.72	8.43	7.80	7.16
Hexafunctional polyester acrylate	4.98	4.33	4.00	3.67
Octyl and Decyl acrylate mixture	22.43	19.48	18.00	16.52
Dispersing agent	4.00	4.00	4.00	4.00
Pigment	20	30	35	40
Total	100	100	100	100

in part on biosourced raw materials. When these polyols were acrylated, we found good performance with some advantages compared to two commercially available controls. These results demonstrate that good performance can be achieved in UV materials manufactured using biosourced intermediates and raw materials.

Experimental

Energy-curable dispersions were made by adding the appropriate amount of pigment and resins to a small glass jar and mixed by hand. The resulting mixture was placed on a three-roll mill (Model 2.5X5; Torrey Hills Technology U.S.A.) for three passes. Dispersibility measurements were done using a BYK-Gardner grind gage using ASTM Method D1316-06. All dispersion had measurements of less than three NPRI. Rheometry measurements were done using an AR 2000 Advanced Rheometer. For yield stress measurements, the stress sweep was run under 0.5 Hz frequency and at 25°C without pre-shear. Other rheological properties—including elastic viscosity and delta curve—were run under different stress and frequency. All color development measurements were done using a Hunter Lab Color Quest XE

FIGURE 1

Yield stress results from black pigment dispersions

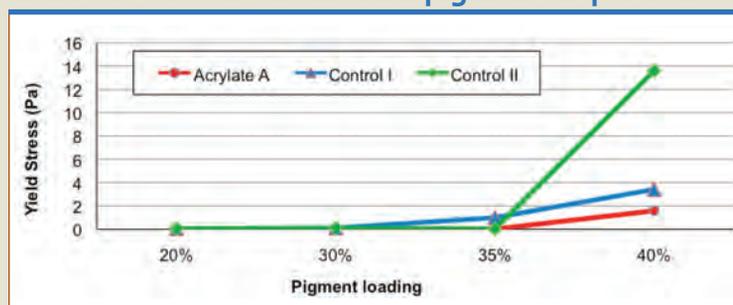
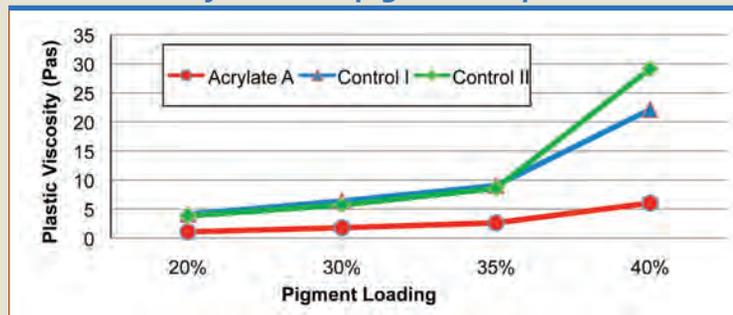


FIGURE 2

Plastic viscosity for black pigment dispersions



spectrophotometer. A KRÜSS K100 surface tensiometer and plate method were used to test the surface tension of the polyester acrylates. Gloss

measurements were done using a BYK-Gardner Micro-TRI-Gloss Meter at room temperature using ASTM Method D523-08.

TABLE 4

Black dispersion formulation using various amounts of dispersing agent (weight percentages are shown)

Material	0% Dispersion Agent	1% Dispersion Agent	2% Dispersion Agent	3% Dispersion Agent
Oligomer	33.96	33.27	32.58	31.89
Tetrafunctional polyester acrylate	8.12	8.04	7.96	7.88
Hexafunctional polyester acrylate	4.17	4.13	4.08	4.04
Octyl and Decyl acrylate mixture	18.75	18.56	18.38	18.19
Dispersing agent	0.00	1.00	2.00	3.00
Pigment	35	35	35	35
Total	100	100	100	100

FIGURE 3

Black dispersion measurements with variable dispersion agent amounts

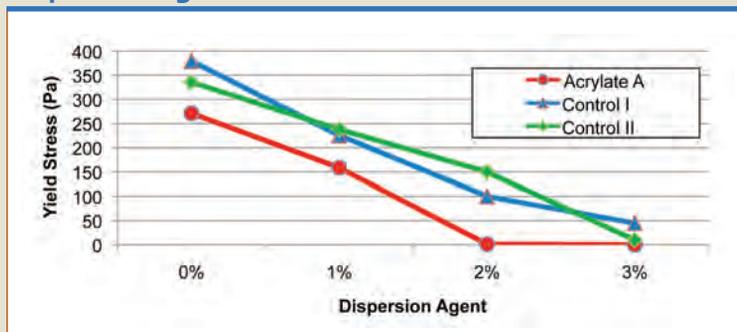
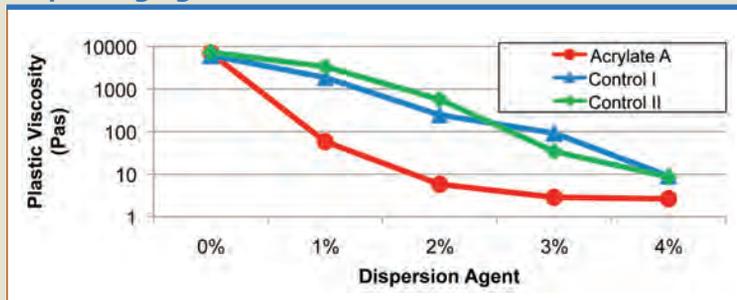


FIGURE 4

Plastic viscosity results using variable amounts of dispersing agent



Results and Discussion

The two new polyols have been developed for use in energy-curable ink dispersions. These polyols were acrylated and evaluated in various flexographic energy-curable formulations. Both polyols incorporate biorenewable raw materials to improve the performance and to help reduce the dependence on petroleum-based raw materials. Table 1 provides the polyol properties.

The first polyol and second polyol in Table 1 were acrylated to make Acrylate A and Acrylate B, respectively. Table 2 summarizes the properties of these new acrylates along with the properties of the two commercial products that were used in comparison studies. The two commercial products used in this evaluation were selected since they are recommended for flexographic UV-ink formulations.

Note that Acrylate A and Acrylate B have relatively low viscosity for polyester acrylates and low surface tension. The low viscosity allows formulators to have broader formulation latitude for energy-curable ink and coating applications. A low surface

tension between 31 and 36 dynes/cm was found with Acrylates A and B.

Acrylate A has a substantially lower viscosity and functionality compared to the two control acrylate resins. Acrylate B has a higher viscosity and functionality compared to Acrylate A, but was lower in viscosity and functionality compared to the two control acrylates.

Pigment Dispersion Evaluation

Yield stress and plastic viscosity were measured in the pigment dispersions with various levels of black pigment. In these experiments, a range of 20-40% black pigment was used to determine how each resin would accommodate an increasing pigment load (Table 3). Commercial tetrafunctional, hexafunctional polyester and an octyl/decyl acrylate mixture were used along with a commercial dispersing agent.

Figures 1 and 2 show the yield stress and plastic viscosity results, respectively.

The yield stress for the Acrylate A formulations was lower in the 40% pigment dispersions compared to the two control dispersions.

The Acrylate A-based dispersion also has approximately three times lower plastic viscosity than the two control-based dispersions. Low viscosity coupled with lower yield stress with higher pigment loading is a desired property in ink formulations, a characteristic that Acrylate A can deliver. These properties can provide a formulator greater latitude to design a suitable pigment dispersion.

Dispersion Agent Reduction

Reducing the amount of additives can reduce the complexity and cost in ink formulations. We have found that Acrylate A can help achieve this goal by reducing the amount of dispersion additive needed for ink dispersions.

FIGURE 5

Yield stress results for the black and blue dispersions using 40% pigment and 4% dispersing agent

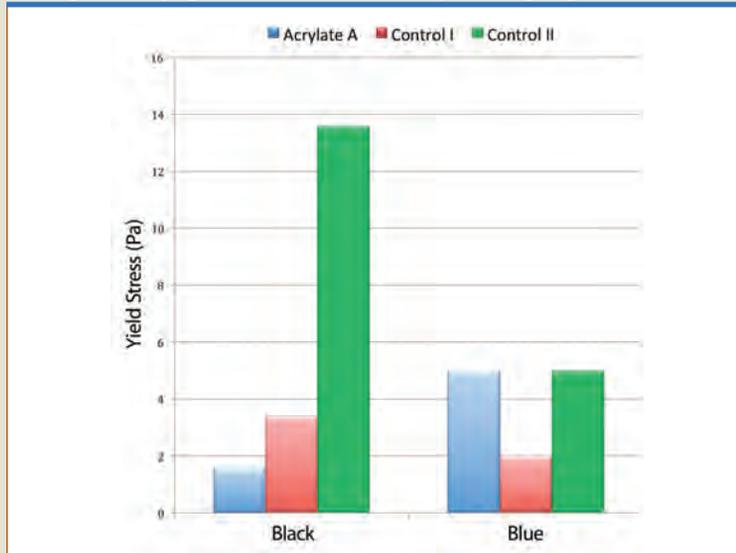


FIGURE 6

Yield stress results for yellow pigment dispersions using 40% pigment and 4% dispersing agent

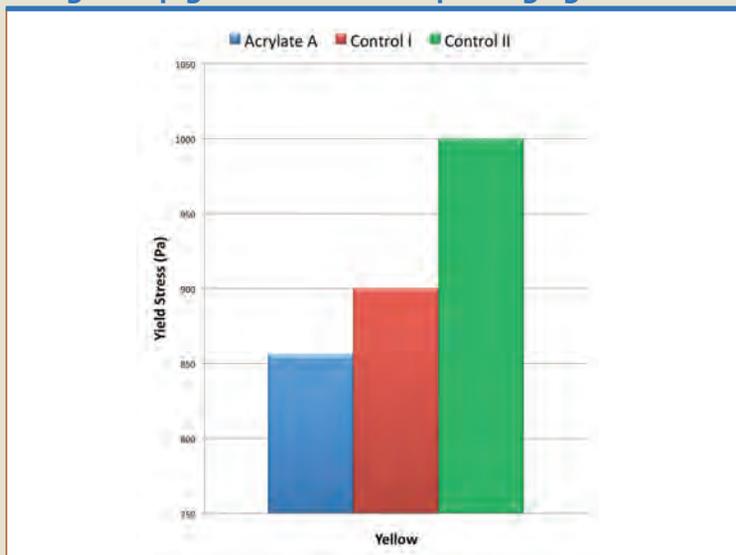


Table 4 shows black ink dispersions made with a set level of pigment (35%) with a range of 0-3% by weight of dispersing agent.

In Figure 3, note that even with no dispersion agent, Acrylate A had a lower yield stress than the two commercial resins. At pigment dispersion levels of 2%,

TABLE 5

Flexographic UV ink formulations

Material	Percentage
Pigment dispersion	50.00
Di-trimethylolpropane tetraacrylate	23.00
Reactive amine coinitiator	5.00
Polyester acrylate oligomer	10.00
Photoinitiator I	3.50
Photoinitiator II	3.00
Photoinitiator III	3.00
Acrylated polysilicone	0.50
Siloxane polyether acrylate	0.50
PTFE dispersion agent	1.00
PE wax	0.50

the yield stress was approximately 100 times lower compared to the commercial resin-based formulations.

The plastic viscosities (Figure 4) decrease quicker for Acrylate A compared to the two controls at the lower levels. The two control plastic viscosities start approaching Acrylate A's performance when the amount of dispersion agent is nearly 4%. From these studies, it is clear that Acrylate A is effectively wetting out the black pigment which results in lower yield stress and plastic viscosity. These experiments illustrate that using Acrylate A in energy-curable dispersions can reduce the amount of dispersion agent needed.

Black, Blue and Yellow UV Ink Dispersions

Black, blue and yellow pigments were evaluated to determine how they would perform with Acrylate A. In these tests, the same formulation shown in Table 3 with 40% pigment and 4% dispersing agent was evaluated for yield stress (Figures 5 and 6).

The black and blue dispersions had significantly lower yield stress

compared with the yellow pigment in these formulations. In the black and yellow dispersions, Acrylate A-based dispersions had lower yield stress compared to the two control dispersions. In the blue dispersion, Acrylate A had approximately the same yield stress as Control II but was higher than the Control I-based dispersion. It is clear that Acrylate A

has better wet-out characteristics and lower yield stress than the commercial resins. Thus, Acrylate A can be used with a variety of pigments to provide a relatively low yield stress as compared with the commercial resins.

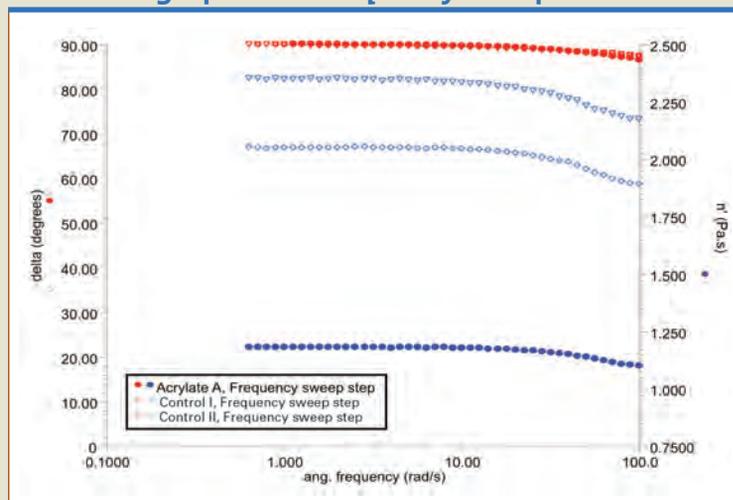
UV Flexographic Ink Formulations

To determine how Acrylate A dispersions perform in flexographic ink formulations, UV black and blue flexographic inks were made and evaluated. Table 5 shows the formulation that was used in all flexographic inks.

A rheological study of the inks was done to evaluate the ink stability and Newtonian behavior during printing under high speed, different speed and press conditions. The frequency sweep testing examines the ink stability at different speed. Stress sweep testing demonstrates the ink stability and delta value change (ratio of viscous and elastic components) on a press. A higher viscous component is more preferred in most ink applications than an elastic component. A higher delta value indicates a better performing ink system.

FIGURE 7

Black flexographic ink frequency sweep results



The dispersions that were used in the flexographic inks contained 4% dispersion agent with 35% pigment. In this study, a black dispersion was used to make the final ink. Figures 7 and 8 show the frequency sweep and stress sweep evaluations for the black ink.

In all of these cases, the formulations using the Acrylate A dispersion had the lowest viscosity. Also, note that in all cases the formulations with Acrylate A dispersion were more stable, especially with blue and black ink, than the two control dispersions under these conditions.

In the case of black flexographic inks, Acrylate A had the lowest and most stable viscosity over various stress levels. It also had nearly Newtonian behavior.

The frequency sweep of the blue flexographic ink is shown in Figure 9.

The rheology profile shows that the Acrylate A-based formulation had a lower, more stable viscosity than the two control-acrylate formulations. The delta value for all three formulations was nearly the same.

In Figure 10, the blue ink formulations were compared. In this case, the earlier black ink results were better than the blue ink results with Acrylate A. Control II-based ink had a better viscosity stability over different stress levels. Also, both inks made with the control resins had better Newtonian behavior than Acrylate A.

After seeing the stress sweep results with Acrylate A with the blue ink, a new polyol was developed (Agent 4087-25) with higher biorenewable content than PC-270-01. This polyol was acrylated to produce Acrylate B. This material had better performance compared to an equivalent UV-curable blue ink formulation using Acrylate A. This blue ink formulation was compared to Acrylate A, Control I and II

FIGURE 8

Stress sweep for the black flexographic ink

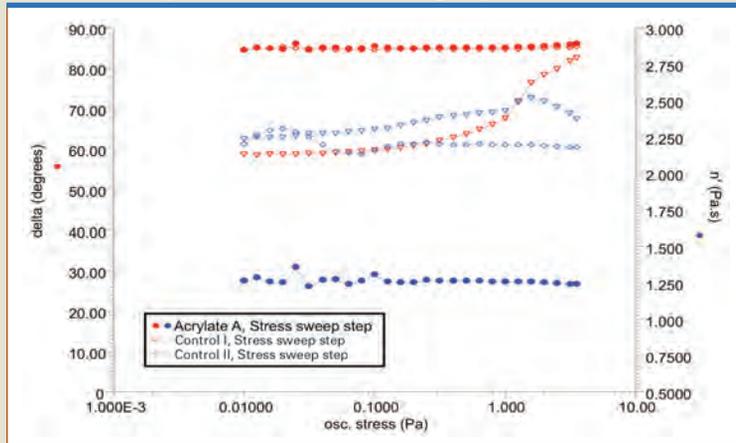
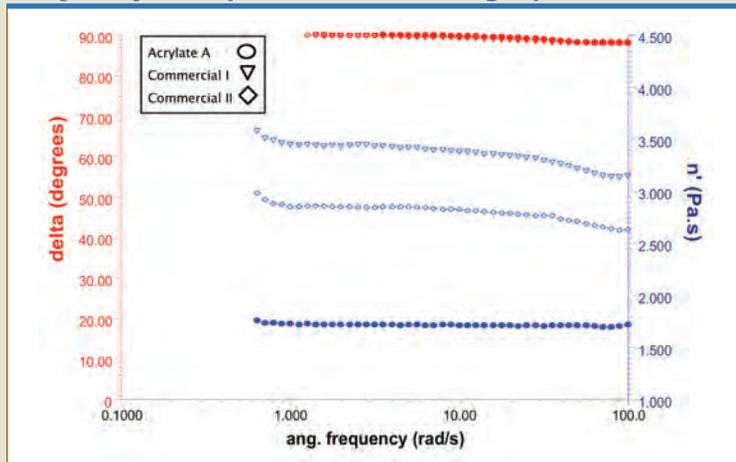


FIGURE 9

Frequency sweep for the blue flexographic ink



formulations in the stress sweep rheological experiment.

Acrylate B has low and relatively stable viscosity as stress is increasing. It also shows better Newtonian behavior compared to Acrylate A and the Control I and II ink formulations. These preliminary results are encouraging and Acrylate B will be thoroughly examined in other formulations.

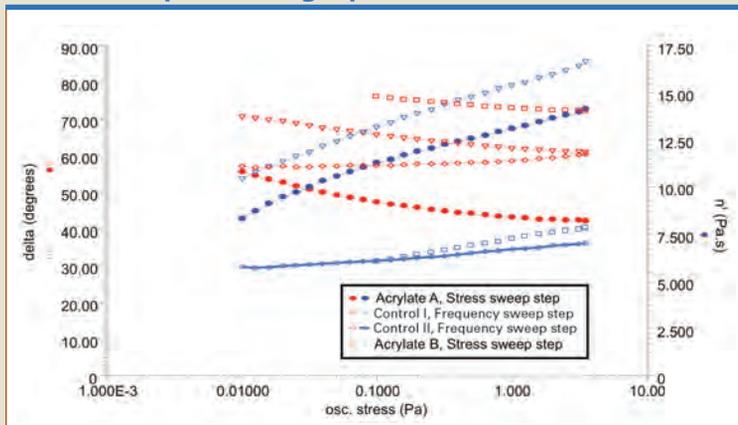
In later experiments with yellow ink, the viscosities of all the samples

were nearly identical and their stability under different stress conditions did not change much. Acrylate A-based inks had behavior that was closer to Newtonian behavior than the two control inks.

The curability of the black, blue and yellow inks made with Acrylate A were compared to Control I and II resins (Figure 11). Samples were prepared using a number 2.5 wired draw down bar on aluminum Q-Panels. The samples were passed through the

FIGURE 10

Stress sweep for flexographic blue formulations



stronger color strength than the Control II formulation. This shows that Acrylate A can, in some ink formulations, enhance color strength. Acrylate A can accommodate high pigment loading in the dispersion while minimizing yield stress and improving the color strength.

Conclusions

This investigation has shown that Acrylate A can be used as an effective resin for energy-curable ink dispersions. Although it has lower functionality and viscosity compared to the two commercial resins, it provided lower yield stress, higher pigment loading and excellent overall

UV-curing machine with a mercury lamp once and immediately tested using a thumbnail test to determine if the ink fully cured.

The cure speed for Acrylate A formulations are nearly the same for the black and yellow inks. For the blue ink, the cure speed was slightly faster with Acrylate A compared to the two control formulations. Thus, Acrylate A has comparable curing speed with the two commercial resins.

The gloss of the cured ink formulations was also measured (Figure 12). Samples were prepared using a number 2.5-wired drawdown bar and cured at 18.2 meters per minute (mpm).

Overall, Acrylate A-based inks had comparable gloss to the two control inks and gave slightly better gloss than the Control II formulation.

Color measurements were also used to evaluate the performance of the ink formulations (Figure 13).

For the black and yellow inks, the Acrylate A formulation had approximately the same color strength as the two control formulations. For the blue ink formulation, Acrylate A had stronger color strength than the Control I formulation and slightly

FIGURE 11

Flexographic in curability speed comparison (meters per minute)

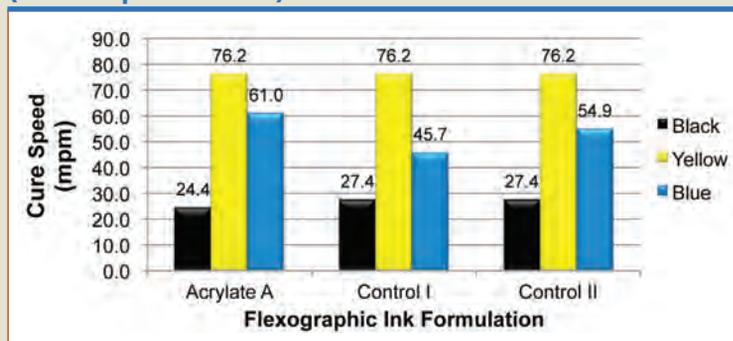
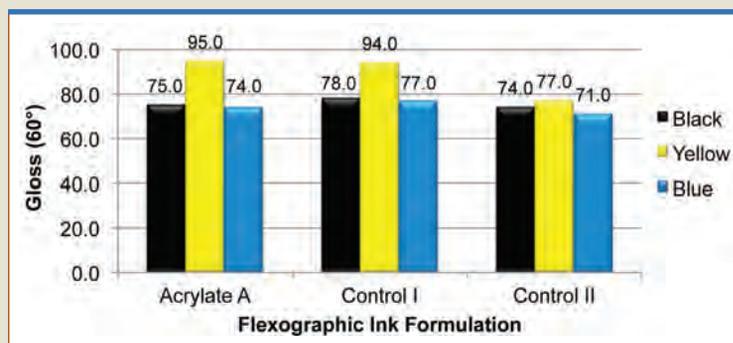


FIGURE 12

Gloss measurements of the UV flexographic in formulations



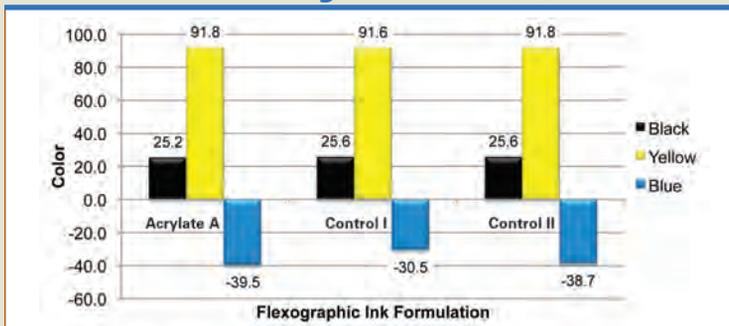
rheological properties. When the acrylate was used in ink formulations, there was no loss of curability, gloss and color strength. Acrylate B also showed very good rheological results in ink formulations. The ability of Acrylate A to effectively wet-out the pigment in UV-ink dispersions has been exhibited and this material can provide the formulator with additional latitude due to its low viscosity, rheological performance and the ability to reduce pigment dispersion agents. ▶

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FIGURE 13

Color strength measurements for the flexographic inks formulations using the Hunter L, a, b Color Scale



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