

# Aqueous Printing on UV Coatings?

## Expanding the Coating Formulator's Possibilities with a Novel, Free-Radical, UV-Curable Polymer

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The vast majority of UV-curable, oligomeric or polymeric materials are defined by modified-acrylated epoxy and urethane resins. While exhibiting excellent mechanical and chemical resistance properties, these materials are generally not receptive to aqueous-based inkjet printing methods.

For such printable surfaces, water-soluble and water-sensitive polymers continue to contribute many

these products into more severe environments in which exposure to water, UV radiation and ozone are common. Thus, for water-soluble materials, the ability to control the degree of cross-linking of the polymer is becoming an increasingly essential requirement.<sup>1</sup>

Cross-linking of water-soluble materials is not without challenges. From identification of suitable cross-linkers and effective cross-linker use levels to coating formulation stabilization (where the cross-linker is present in the solution) and safe handling of such materials for plant personnel, the implementation of cross-linking technology can be a challenge. One potential approach to addressing many of these issues is the implementation of UV-coating technology.

A distinctive advantage of UV technology is that properly designed coating solutions are unlikely to change in the absence of appropriate light. This provides a tool for greater control of the coating components and production processes.

Commercial UV-coating applications can be found on a variety of substrates such as wood, metal, paper, plastics,

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important properties to the final, inkjet receptive coating product. These materials, for example, can provide enhanced critical printable coating properties such as dye fixation, gloss, and fluid management of print ink/solvent. Unfortunately, the water sensitivity can also bring serious challenges to the performance of the final, printed coating. This can be perceived negatively, especially when the industry trend is to extend

ceramics/glass and textiles. As V.P. Thalacker wrote back in 1990... "in addition to the performance attributes radiation-curable coatings are capable of providing, such technology can be attractive when reduction in energy costs and elimination of solvents (VOC content) are desired."<sup>2</sup> Now some 20 years later, those comments are even more powerful in the face of ever rising energy costs and increasing pressures to improve the environmental footprint of many manufacturing processes. More recently, in 2006, an executive summary from the Specialty Graphic Imaging Association encouraged members of the graphic arts community to achieve energy reduction via radiation-curing technology to enhance the sustainability of graphic-related products.<sup>3</sup>

This article will focus on a novel technique for cross-linking cationic, water-soluble, inkjet receptive polymers—specifically, poly(vinylcaprolactam-co-vinyl pyrrolidone-co-(dimethylamino) ethyl methacrylate), modified with glycidyl methacrylate (VCL/VP/DMAEMA/GMA). The structure and properties of this novel material are presented. In addition, some formulation strategies for inkjet receptive coatings are discussed and examples listed. The results are discussed in the context of potential directions for future coating design work.

## Experimental

The preparation of VCL/VP/DMAEMA/GMA is presented elsewhere and beyond the scope of this paper.<sup>4,5</sup> This acrylated polymer was used at 25% wt/wt in 2-hydroxyethyl acrylate for formulation purposes. Methoxy polyethylene glycol (350) monomethacrylate is available under the trade name CD551 from Sartomer. 2-Hydroxyethyl acrylate (HEA, 97% purity), [2-(Methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium

hydroxide (betaine, 97% purity) and acrylic acid (AA, 99% purity) were purchased from Aldrich Chemicals, located in Milwaukee, Wisc. Darocur 1173 is 2-hydroxy-2-methyl-1-phenyl-1-propanone is available from Ciba Specialty Chemicals, located in Tarrytown, N.Y.

To test the UV-curable VCL/VP/DMAEMA/GMA polymer, a coating solution is prepared. This coating solution was drawn onto clear, DuPont-Teijin Melanex 4 mil clear polyester film using a #3 Meyer rod. The resulting wet film is placed into a Fusion UV LC-6B bench-top conveyor equipped with F300S/SQ lamp system. The belt speed was set for 12 ft./min. The approximate dose is 1,500 mJ/cm<sup>2</sup> and the intensity is 4.6 W/cm.<sup>2</sup> An inkjet test pattern was printed onto the film using the Hewlett-Packard HP D2430, in Plain Paper Mode (Palo Alto, Calif.) or an Epson R280, in Plain Paper Mode (Nagano, Japan). Optical density was measured using a Gretag Macbeth D19C Densitometer (Regensdorf, Switzerland). Gloss was measured at 60° using a BYK micro-TRI-gloss meter (Model 4430; Geretsried, Germany) when coating was applied to white Melanex film. The printed film was allowed to stand for a minimum of

24 hours. Portions of the printed film were also subjected to a distilled water, agitated 1-minute submersion test.

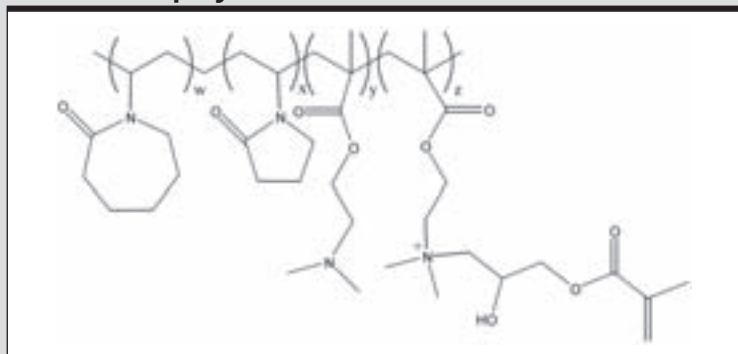
## Results and Discussion

Previous work demonstrated the excellent print receptivity of the cationic VCL-co-N-[ $\beta$ -(dimethylamino) propyl]methacrylamide (DMAPMA)-co-2-hydroxyethyl methacrylate (HEMA) polymer coupled to strong water solubility.<sup>1</sup> This polymer, when cross-linked with a proper amount of poly-functional aziridine, exhibits a strongly improved water resistance. Subsequent work demonstrated that modifying the VCL/DMAPMA/HEMA polymer with GMA also presented good potential for inkjet printability in the presence of an alternate cross-linking technique, in which curing is achieved in the presence of free radicals.<sup>6</sup> From a physical property coating perspective, however, the VCL/DMAPMA/HEMA base polymer does tend to exhibit brittle character which can require some additional formulation attention.

VCL/VP/DMAEMA is another excellent water-soluble and print-receptive polymer but tends to be more flexible and adhesive. It is also less cationic than the VCL/DMAPMA/

## FIGURE 1

### Proposed structure of VCL/VP/DMAEMA/GMA UV-curable polymer



HEMA/GMA polymer. To render this polymer suitable for UV cross-linking, the base polymer was acrylated with GMA. A representation of the proposed structure for VCL/VP/DMAEMA/GMA is presented in Figure 1.

The physical properties of the VCL/VP/DMAEMA/GMA polymer are presented in Table 1. In general, the polymer is a low-viscosity material that exhibits a reasonably high  $T_g$ . In addition to the previously mentioned properties, the polymer also exhibits high gloss, transparency, film-forming and dye-fixation properties.

### 100% Solid, Nonaqueous-based UV Coating, Epson

A nonaqueous, prototype glossy coating formulation was developed for the Epson printer and is presented in Table 2. The basic compositional strategy for this coating was to enhance Epson ink penetration into the VCL/VP/DMAEMA/GMA polymer by utilizing methoxy polyethylene glycol (350) monomethacrylate. The methoxy polyethylene glycol (350) monomethacrylate aids the Epson print but is not capable of any functional dye binding. The methoxy polyethylene glycol (350) monomethacrylate also tends to reduce the general adhesiveness of the coating. The betaine and acrylic acid are employed to open the network structure, enhancing the swelling nature of the coating. Darocur

TABLE 2

### Prototype nonaqueous-based, UV-curable coating

Property	Mass (g)	Percent Solids	Dry Mass (g)	Wt% Dry Film Composition
VCL/VP/DMAEMA/GMA	2	100	2	13.1
2-Hydroxyethyl acrylate	6	100	6	39.2
Methoxy polyethylene glycol (350) monomethacrylate	4	100	4	26.1
Betaine	1	100	1	6.5
Acrylic Acid	2	100	2	13.1
Darocur 1173	0.31	100	0.31	2
<b>Total</b>	<b>15.31</b>		<b>15.31</b>	<b>100</b>

1173 initiates the UV free-radical polymerization process. This coating yields print receptivity, gloss and transparency.

As a general overview to coating preparation, ingredients were combined in the following manner. First, VCL/VP/DMAEMA/GMA in HEA is combined with methoxy polyethylene glycol (350) monomethacrylate during gentle warming. The betaine and acrylic acid are added in a separate container and mixed with gentle warming until fully solvated. Then the betaine/acrylic acid blend was added dropwise to the VCL/VP/DMAEMA/GMA in HEA and methoxy polyethylene glycol

(350) monomethacrylate solution. Finally, Darocur 1173 initiator was added. During all stages of formulation construction, the fluid was thoroughly mixed. Specific coating compositional details are presented in Table 2.

The properties for the prototype coating and coating solution are presented in Table 3. The solution properties are suitable for a variety of commercial application methods, including knife, rod, slot-die and blade process. Other processes (such as gravure) may require some additional compositional modifications to present a more appropriate solution viscosity.

These results support the desirable transparency and gloss requirements for printable coatings. The coating is soft and not very abrasion resistant. The incorporation of modest amounts of fumed silica may help improve abrasion resistance. Upon a sharp folding, the coating exhibited good cracking resistance. As expected, by incorporation of more than 25% methoxy polyethylene glycol (350) monomethacrylate into the coating, the adhesion decreased to an unsatisfactory level on polyester. An

TABLE 1

### Physical properties of VCL/VP/DMAEMA/GMA UV-curable polymer

Property	Data
Viscosity (cPs) (25% in HEA)	~18,000
Molecular Weight (g/mol)	~80,000
$T_g$ (°C)	~160°C
K-Value range	44-50

TABLE 3

**100% solid, nonaqueous-based UV coating, Epson**  
**Properties of nonaqueous prototype**  
**UV-curable coating**

Property	Data
Solution Solids (%)	100
Coating Solution Viscosity (cPs)	4900 (Brookfield LV III, #64, 100 RPM)
Coat Weight ( <i>grams per square meter</i> )	30
Appearance	Transparent
Gloss (60°) (White Melanex)	90
Pencil Hardness	6B
Tabor Abrasion	<20 cycles
MEK Rubs	Hazy at 30 rubs
Adhesion on polyester	Peels/poor

dye-binding properties of the coating in the presence of water. To improve the print ink penetration into the coating, methoxy polyethylene glycol (350) monomethacrylate was increased, but to a minimal level. However, at more than 25% of the coating, the net result appears to be a significant decrease in the coating's dye-binding capacity. Improving the performance of this coating approach would require enhancing the cationic nature of the film, perhaps by blending a more cationic, acrylated lactamic polymer. More work is required to confirm this theory.

**100% Solid, Nonaqueous-based UV Coating, HP**

A nonaqueous, prototype glossy coating formulation for the HP printer was developed and is presented in Table 5. The basic compositional strategy for this coating was to enhance HP ink penetration into the VCL/VP/DMAEMA/GMA polymer by balancing the levels of betaine, 2-hydroxyethyl acrylate and acrylic acid. Note that this time, methoxy polyethylene glycol (350) monomethacrylate was not required to achieve acceptable print performance. The betaine, 2-hydroxyethyl acrylate and acrylic acid adjust not only the coating composition

TABLE 4

**100% solid, nonaqueous-based UV coating, Epson**  
**Print properties of nonaqueous prototype**  
**UV-curable coating**

Color	Optical Density Before Water Exposure	Optical Density After Water Exposure	% Change
K (Black)	2.3	0.64	-72
C (Cyan)	0.6	0.08	-86
M (Magenta)	1.3	0.13	-90
Y (Yellow)	1.2	0.56	-53

alternative to this coating approach may be to incorporate triethylene glycol divinyl ether (DVE-3) or cyclohexane dimethanol divinyl ether (CHVE), at the expense of methoxy polyethylene glycol (350) monomethacrylate, to help enhance the adhesive properties.

Print test results for the prototype coating are presented in Table 4.

Visually, the printed surface revealed generally good print uniformity and performance, suggesting good dye-binding properties. However, the magnitude of % change after water submersion reveals limitations to these

TABLE 5

**Prototype nonaqueous-based, UV-curable coating**

Product	Mass (g)	Percent Solids	Dry Mass (g)	Wt% Dry Film Composition
VCL/VP/DMAEMA/GMA	2.03	100	2.03	13.9
2-Hydroxyethyl acrylate	7.07	100	2.08	48.8
Betaine	2.08	100	2.08	14.4
Acrylic Acid	4	100	4	27.6
Darocur 1173	0.31	100	0.31	2
<b>Total</b>	<b>14.49</b>		<b>14.49</b>	<b>100</b>

**TABLE 6**

**100% solid, nonaqueous-based UV coating, HP  
Properties of nonaqueous prototype  
UV-curable coating**

Property	Data
Solution Solids (%)	100
Coating Solution Viscosity (cPs)	8000 (Brookfield LV III, #63, 10 RPM)
Coat Weight (grams per square meter)	56
Appearance	Transparent
Gloss (60°) (White Melanex)	90
Pencil Hardness	B
Tabor Abrasion	<20 cycles
MEK Rubs	No effect
Adhesion on polyester	100%

**TABLE 7**

**100% solid, nonaqueous-based UV coating, HP  
Print properties of nonaqueous prototype  
UV-curable coating**

Color	Optical Density Before Water Exposure	Optical Density After Water Exposure	% Change
K (Black)	3.2	3.0	-6.3
C (Cyan)	1.3	0.8	-38
M (Magenta)	1.3	0.93	-28
Y (Yellow)	0.5	0.5	0

but also alter the network structure, enhancing the swelling nature of the coating. Darocur 1173 was employed to initiate the free-radical polymerization. This coating yields print receptivity, gloss and transparency.

As a general overview to coating preparation, ingredients were combined in the following manner. First, VCL/VP/DMAEMA/GMA in HEA is combined. The betaine and acrylic acid are added in a separate container

and mixed until fully solvated. Then the betaine/acrylic acid blend is added dropwise to the VCL/VP/DMAEMA/GMA in HEA solution. Finally, Darocur 1173 initiator was added. During all stages of formulation construction, the fluid was thoroughly mixed. Specific coating compositional details are presented in Table 5.

The general properties for the prototype coating and coating solution are presented in Table 6. The general

solution properties are suitable for a variety of commercial application methods, such as knife, rod, slot-die and blade process. Other processes (such as gravure) would likely require some additional compositional modifications to present a more appropriate solution viscosity.

These results support the desirable transparency and gloss requirements for printable coatings. The coating is soft and not very abrasion resistant. The MEK rub resistance is superior to the first coating. The adhesion to polyester was good. Upon a sharp folding, the coating exhibited some “spider cracking.” The flexibility may be improved by including a minor amount of triethylene glycol divinyl ether (DVE-3). Print test results for the prototype coating are presented in Table 7.

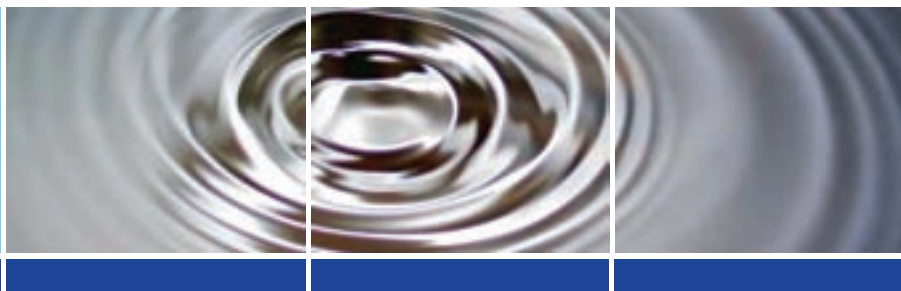
Unlike the results presented in Table 4, data found in Table 7 suggest good dye-fixation properties. By studying the interrelationships of the monomers, we were able to locate a general compositional region to not only receive the water-based ink more efficiently but also enabled improved dye and pigment binding capacity. Now that this space has been identified, it is possible to envision improving the performance by further modification to the cationicity of the resin. However, this coating is currently quite interesting for performance on the HP printer.

**Conclusions**

We have successfully developed and demonstrated a free radically curable, cationic, inkjet receptive polymer. Properties of this novel polymer were presented. Aqueous and nonaqueous prototype coatings have been developed and the general formulation strategies discussed. While

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some improvements are required to make a commercially viable system, these prototypes clearly demonstrate functional possibilities for novel UV-coating systems. ▶

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