Radiation-Curable Inks and Coatings from Novel Multifunctional Acrylate Oligomers

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Abstract

Families of multifunctional acrylate oligomers have been developed which are useful as pigment grinding and let-down vehicles for radiation-curable ink formulations and over-print varnish (OPV) applications. Multifunctional acrylate resins are formed by the reaction of acrylate monomers and oligomers with β-dicarbonyl compounds (Michael "donors") that can participate in the Michael addition reaction. These resin vehicles have a built-in photo-labile chromophore, enabling ink formulations made from their dispersions to cure under standard UV-cure conditions with significantly less photoinitiator than commercial formulations. OPV formulations have been developed that cure without the addition of traditional photoinitiator. The resins also exhibit excellent pigment wetting characteristics and can be designed to function as a single dispersion or let-down vehicle for different pigments as well as for different ink applications such as screen, flexographic, and lithographic printing. Resin design, ink and OPV formulations, UV cure performance and properties of the prints are discussed.

Introduction

Increased emphasis on environmental protection is a driving force advancing the utilization of energy-curable ink technology in the printing and graphic arts industry. Energy-curable inks include ultraviolet light (UV) curable and electron beam radiation (EB) curable inks.

Achieving good quality UV ink performance is strongly correlated with the final rheology of the formulated ink system. To a great extent, rheology is determined by the conformation adopted by the resin "vehicle" when wetting the surface of pigment particles. Stable dispersion of the pigment in ink formulations, good ink flow and transfer on press, and subsequent color strength all depend upon good pigment wetting.

The rheological advantages of a well-dispersed system are good flow, low overall ink viscosity (depending on the application), high gloss and proper color development. UV-curable oligomers with adequate pigment wetting characteristics are available commercially. Advances in raw material technology have made it possible to formulate inks which can UV cure at commercial line speeds to give prints with good opacity, durability and chemical resistance. In recent years, environmental concerns regarding the use of volatile solvents in "traditional" inks, financial considerations, and the availability of alternative technologies, have all combined to persuade printers to consider UV printing as a viable, cost-effective option.

Commercial UV inks require substantial quantities of mixed photoinitiators to ensure optimum cure and to develop proper adhesion in the printing processes. These photoinitiators are typically low molecular weight compounds that can produce volatile or toxic byproducts after decomposition and which may come into contact with skin and eyes. Traditional photoinitiators can also be expensive, malodorous, and may contribute to film yellowing, which can limit their applicability, in general, and may render them unsuitable for use in white and light-colored inks. Functionalized oligomeric photoinitiators may overcome some of these drawbacks. However, multi-step syntheses may be required in their manufacture, low functionality may be detrimental to reactivity and final properties, and catalyst or initiator may still be required to effect adequate cross-linking.

The amount of traditional photoinitiator in ink formulations can be significantly reduced by using the acrylate oligomer technology described in this paper and elsewhere[1-3]. This new acrylate oligomer technology produces uncrosslinked resins via the Michael reaction of β-dicarbonyl compounds with multifunctional acrylates. These multi-functional polyacrylate oligomers have dual chemical functionality: polymerizable acrylic groups and a labile ketone group that is capable of dissociating, upon exposure to UV radiation, to initiate free radical polymerization of the oligomer.

In an acrylate/acetoacetate Michael addition synthesis the resulting product has an increased molecular weight compared to the parent acrylate(s). This provides resins with reduced volatility and propensity for skin irritation. The chemistry and process utilized to produce these self-initiating resins allows for outstanding control of the final product including composition, molecular weight, functionality, architecture and incorporation of alternate functionality. The synthesis is versatile and robust, enabling the production of customized resin structures. Virtually a limitless number of acrylate oligomers can be made with this novel resin technology.

This paper describes the advantageous use of these resins alone, or modified by reaction with and/or blending with additional materials, for grinding different color pigments. The resulting pigment dispersions can be let-down with appropriate oligomers based on the same Michael reaction technology to give UV-curable screen, flexographic, ink-jet and lithographic inks. Low viscosity resins based on this technology can be used in OPV applications to eliminate or significantly reduce the amount of photoinitiator required for cure at high line speeds.

Ink formulations based on these novel photocurable Michael resins can incorporate a nearly unlimited variety of additives due to the chemical/architectural control possible in their synthesis. Thus, many more options are available to the formulator who must address challenges specific to each printing application.

Experimental

Acrylic monomers and oligomers were provided by UCB Chemicals, Sartomer, Rahn Chemicals and AKZO Resins. Ethyl acetoacetate (EAA) and pentanedione (PD) were purchased from Eastman Chemical and other Michael donors were provided by Lonza AG. Diethanol amine was purchased from Aldrich Chemical Co. Infrared analyses were performed on a Nicolet 5-Series FTIR. The viscosities of various resins as well as ink formulations were measured at 25 ^{o}C using a Brookfield CAP 2000L viscometer. Oligomer syntheses were monitored by change in refractive index measured using a Rudolph Research Analytical J157 refractometer at 25 ^{o}C.

Typical resin syntheses were performed by combining acrylic starting material(s), Michael donors, and catalyst at room temperature with stirring. The reaction was heated to 95 ^{o}C and held at that temperature until conversion of ethyl acetoacetate was complete using refractive index and viscosity measurements. The reaction product was cooled and a secondary amine added to cap some of the acrylate groups.

Pigments were dispersed in the resins using a Hauschild mixer followed by grinding on a table-top Lehmann 3-roll mill. Application of the screen inks to a variety of substrates was accomplished by using a suitable screen mesh mounted to give a defined clearance and a hand-held squeegee. A pre-stretched aluminum frame of size 20 X 24 square inches was used with a mesh count of 305. A 70 durometer aluminum squeegee was used to screen print on to various substrates. Flexographic printing was simulated using a hand-proofer equipped with 2.8 bcm anilox roll. Over-print varnishes were applied in the same manner. A “quick-peek” apparatus was used to simulate lithographic printing in the bench-marking studies. Emulsion behavior of the off-set inks was studied using a hydroscope. All pigment dispersion viscosities were measured at 50 rpm.

Irradiation of samples was performed on a Fusion UV cure unit equipped with a 600W/in.H-bulb at the doses specified. Tack was assessed by rubbing a cotton swab over the cured surface. Ink and OPV performance properties were measured by a variety of different test methods. Gloss was measured using a BYK Gardner model 4520 Micro-TRI-Gloss meter (BYK-Gardner USA, Columbia, Md.) with a coated substrate placed on black felt. The light source utilized was 60° based on ASTM D523-89. Adhesion of the experimental inks to substrates was measured according to the crosshatch method of ASTM 2359. The test reports values OB to 5B; OB being a total failure and 5B comprising excellent adhesion.

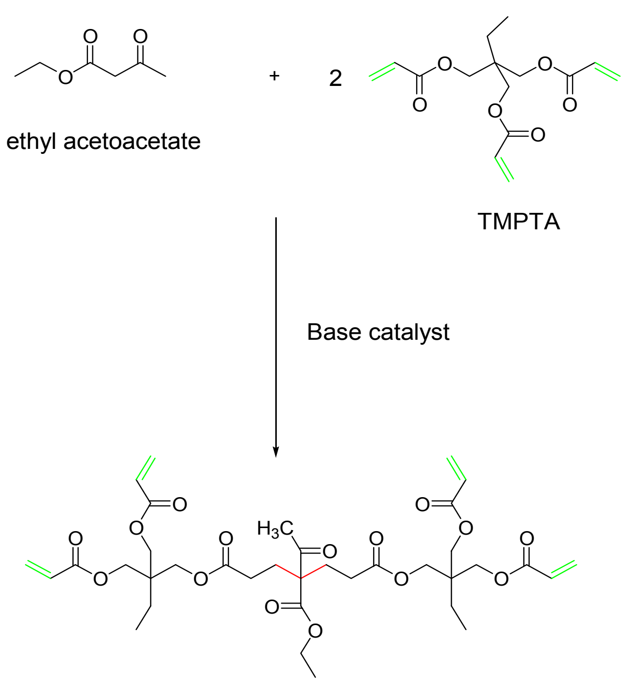
Results and Discussion

Synthesis of Resin – Chemistry & Resin Design Flexibility

From a design perspective, Michael oligomer technology is broad and readily lends itself to the preparation of novel acrylic materials. Self-initiating resins are formed by the Michael addition reaction of a Michael donor (e.g. ethyl acetoacetate) with a Michael acceptor (acrylate) in the presence of a basic catalyst. Figure 1 shows the synthesis of a multifunctional acrylic resin in which TMPTA is combined with EAA in a 2:1 ratio to form the tetrafunctional product. In the making of these novel oligomers, the acrylates utilized can be of any functionality (e.g., monoacrylate, diacrylate, triacrylate, etc.), or of any class (e.g., acrylic monomers, epoxy acrylate oligomers, urethane acrylate oligomers, polyester acrylates, etc.). Also, combinations of the above mentioned acrylate building blocks can be used to generate materials with a blending of the structural features and performance characteristics of each of the components.

Functionality and equivalent weight can be tailored by choice of starting material. Molecular weight of the desired product can also be varied and controlled by the choice of Michael donor and Michael acceptor, and the reactant ratio used in the synthesis.

Figure 1. Example synthesis of a 4-functional branched oligomer.



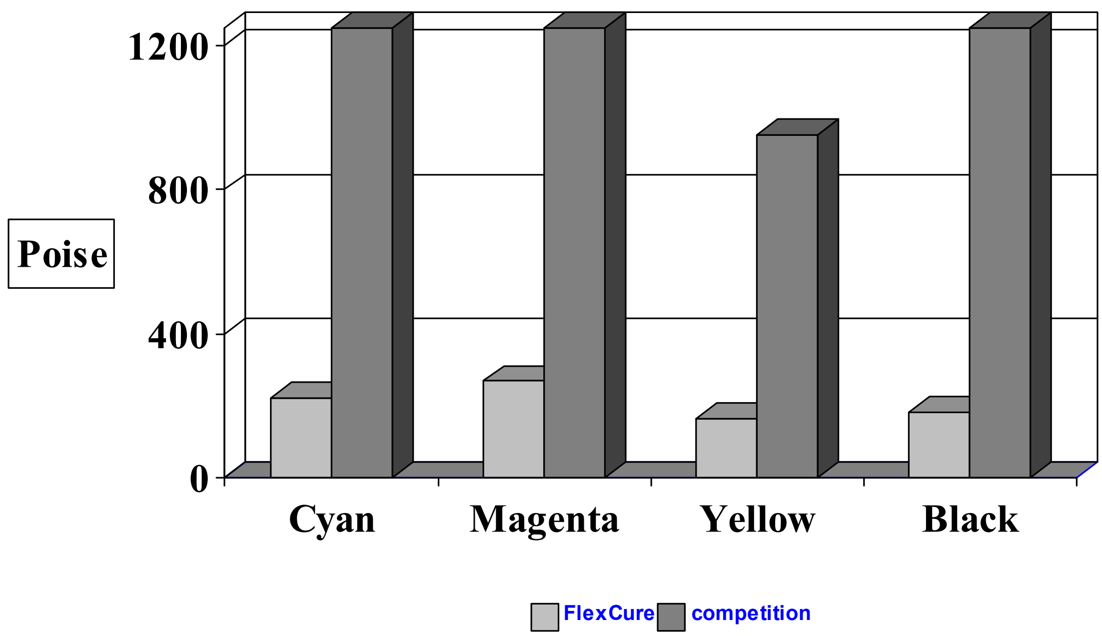
Beyond the broad resin design flexibility, the most outstanding performance feature of these resins is that they "self-initiate" upon UV irradiation. The dose needed to cure the un-pigmented neat resins without photoinitiator ranges from less than 100 mJ/cm^2 to 3000mJ/ cm^2, depending on selection and structure of the starting materials. Low levels of added photoinitiator can reduce dose to tack-free cure even further.

Pigment Grinding Vehicle

This novel technology can be readily applied to make single resins functioning as pigment grinding vehicles for radiation-curable ink applications. A number of such resins have been designed and synthesized for the purpose of pigment grinding. They are characterized by excellent pigment dispersing ability and exhibit higher throughput and lower viscosity compared to commercial vehicles. Thus higher pigment loadings are possible with a minimum amount of diluent monomer using these resin vehicles.

The dispersing resins were benchmarked against commercial resins using lithol rubine, phthalo blue, AAA yellow and pigment black 7 at a 30% loading in the dispersions. Grind performance was evaluated after 10 passes on a table-top Lehmann 3-roll mill. Figure 2 demonstrates the significant advantages in pigment grind viscosity versus "standard" grinds.

Figure 2: Viscosity comparisons for pigment dispersions



While Figure 2 illustrates the relative viscosities of the pigment dispersions, Table 1 summarizes the dispersion quality and color development properties measured by a clear bleach test. Ashland FlexCure™ oligomer resins have better grindability and pigment wetting characteristics comparable to conventional vehicles. Higher pigment loading levels are possible with these resins when using a 3-roll mill. Also, NPIRI grind gauge evaluations indicate that fewer passes are required to grind pigments in the new Michael oligomer resins compared to the standard. This is a distinct process advantage. A further advantage is obtained because the new resins are self photo-initiating, thus reducing significantly the photoinitiator loading in ink formulations derived from these dispersions.

Table 1: Benchmarking of pigment dispersions

Formulation	**Pigment Loading**	**NPIRI Grind**	**L**	**a***	**b***	**60^o Gloss**
FlexCure™ D30 Self-Initiating Resin	30% Blue	No Scratch No Pepper	58.28	-31.07	-39.23	83.4
Competitive Benchmark	30% Blue	Scratch at 7 Medium Pepper	57.21	-30.31	-40.29	83.5
FlexCure D30 Self-Initiating Resin	30% Red	No Scratch No Pepper	46.67	55.44	4.33	79.7
Competitive Benchmark	30% Red	Scratch at 6 Lots of pepper	49.25	54.97	0.28	78.3
FlexCure D30 Self-Initiating Resin	30% Yellow	No Scratch No Peppers	86.43	-6.31	80.45	86.7
Competitive Benchmark	30% Yellow	No Scratch Lots of Peppers	86.59	-6.62	79.58	85.7
FlexCure D30 Self-Initiating Resin	30% Black	No Scratch No Peppers	26.02	0.46	0.19	85.0
Competitive Benchmark	30% Black	Scratch at 2 Lots of Peppers	24.67	0.42	0.10	79.0

Screen Inks

Advances in raw material technology have made it possible to formulate screen inks which can UV cure at commercial line speeds to give prints with good opacity, durability and chemical resistance. A substantial amount of mixed photoinitiators is required to ensure surface and through cure in a thick film application such as screen printing. Screen-printing inks based on the novel acrylate oligomers described in this paper offer significant advantages over inks based on traditional multifunctional acrylic monomers, as described above. A typical screen ink formulation based on Ashland Michael resin technology is represented in Table 2.

Table 2: Typical screen ink formulation

Description	Parts (w/w)
30% blue pigment dispersion w/ FlexCure™ D30 self-initiating resin	13.4
FlexCure S510 self-initiating resin	71.6
adhesion promoting monomer	10.0
reactive foam control agent	1.0
silicone foam control agent	0.5
photoinitiator package	3.5

Screen inks based on the new oligomer technology were benchmarked against commercial inks under identical experimental conditions. Particular effort was made to replace only the oligomer and monomer portions of the benchmark formulations so that the formulations comprising the self initiating resin technology could be better compared and contrasted with the standard technology.

Industry standard pigments were chosen to compare the UV-cure resins of the present invention against conventional UV-cure resins. Titanium Dioxide White DuPont R-706, Pigment Yellow 14 YE 1400 DC (diarylide yellow, Magruder Color Company), Pigment Blue 15:3 BL-1531 (phthalocyanine blue, Magruder Color Company) and Pigment Red 57:1 LR-1392 (metallized azo red, Magruder Color Company) were the pigments selected for this study. Formulation viscosity was measured and deemed acceptable as long as it matched the standard yellow ink formulation within a tolerance of 10%. Comparative evaluations of the screen ink formulations are summarized in Table 3.

Table 3: Comparative evaluation of screen-ink formulations

Formulation	Pigment (% by weight)	% PI	Dosage to tack-free cure (mJ/cm^2)	60º Gloss	Adhesion (coated paper)
FlexCure S510 Self-Initiating Resin	40 (White)	2.0	<300	89.6	5B
Competitive Benchmark	40 (White)	6.0	<300	90.9	5B
FlexCure S510 Self-Initiating Resin	4 (Yellow)	2.5	<300	95.1	5B
Competitive Benchmark	4 (Yellow)	4.0	<300	92.8	5B
FlexCure S510 Self-Initiating Resin	5 (Red)	3.5	<300	93.0	5B
Competitive Benchmark	5 (Red)	5.0	<300	88.0	5B
FlexCure S510 Self-Initiating Resin	4 (Blue)	3.5	<300	89.7	5B
Competitive Benchmark	4 (Blue)	6.0	<300	35.3	5B

The examples listed in the above table contrast the performance of the various color screen-printing inks formulated with Michael oligomer resins and commercial vehicle expressly developed for screen ink formulations. An obvious advantage of ink formulations based on self-initiating Michael resins over the commercial standards is the much lower photoinitiator requirement of the former to achieve comparable gloss and adhesion levels. This advantage translates into significant cost savings as well as providing handling benefits from using less of the traditional photoinitiators. Also, gloss performance of the experimental inks described above, are generally better than the commercial benchmarks at much lower levels of photoinitiator.

Flexographic Inks

In recent years, UV flexographic inks have been developed as a high quality, high productivity alternative to offset or letterpress printing inks as well as solvent and water-based flexographic inks. Advances in raw material technology have made it possible to formulate flexo inks which have the high pigment loadings and good flow characteristics that are needed in the ink fountain, to enable the ink to transfer cleanly from the anilox roll, as well as to print with high color density from fine line aniloxes. In addition, better flow properties lead to a better printed appearance, as the ink will level more completely and yield good gloss.

Commercial UV-cure flexo inks require the use of substantial quantities of a mixture of different photoinitiators to ensure optimum cure and to obtain proper adhesion. The flexographic inks based on new self-initiating resin technology can UV-cure at commercial line speeds to give prints with good opacity, durability, and chemical resistance at lower photoinitiator levels. A typical flexographic ink formulation is represented in Table 4.

Table 4: Typical flexographic ink formulation

Description	**Parts (w/w)**
30% pigment dispersion w/FlexCure™ D30 self-initiating resin	28.1
FlexCure F130 self-initiating resin	56.9
adhesion promoting monomer	10.0
reactive foam control agent	1.0
silicone foam control agent	0.5
photoinitiator package	3.5

As in the screen ink formulation examples, the flexographic inks based on the new technology were benchmarked against commercial inks, making particular effort to replace only the oligomer and monomer portions of the benchmark formulations. The same pigments used in the screen ink formulations were used for this benchmarking example. Formulation viscosity was measured and deemed acceptable as long as it matched the standard ink formulation within a tolerance of 10%. Comparative evaluations of the flexographic ink formulations are listed in Table 5.

Table 5: Comparative evaluation of flexographic ink formulations

Formulation	Pigment (% by weight)	% PI	Dosage to tack-free cure (mJ/cm^2)	60º Gloss	Adhesion (coated paper)
FlexCure™ F177 Self-Initiating Resin	40 (White)	3.0	<300	84.2	5B
Competitive Benchmark	40 (White)	5.0	<300	53.0	5B
FlexCure Self-Initiating Resin	9 (Yellow)	3.5	<300	64.2	5B
Competitive Benchmark	9 (Yellow)	5.0	<300	57.1	5B
FlexCure Self-Initiating Resin	9 (Red)	3.5	<300	79.8	5B
Competitive Benchmark	9 (Red)	4.5	<300	72.0	5B
FlexCure Self-Initiating Resin	9 (Blue)	5.0	<300	65.8	5B
Competitive Benchmark	9 (Blue)	6.0	<300	43.3	5B

The examples listed in the above table contrast the performance of the various color flexographic printing inks formulated with self-initiating resins and commercial vehicle expressly developed for flexographic ink formulation purposes. An obvious advantage of ink formulations, based on resins built with FlexCure Michael resin technology, over the commercial standards is the lower photoinitiator requirement of the former to achieve improved gloss and comparable adhesion levels. This advantage translates into both significant cost savings and handling benefits.

Lithographic Inks

Lithography is the most widely used printing process which employs UV and EB inks. Various substrates including paper, carton board, metal, plastic and laminates can be printed by this method. The advantages of using UV inks in this process are that they are cleaner and easier to handle than conventional lithographic inks. Conversely, they are less versatile in terms of their ink/water balance, when running on a press. Printing requirements for offset lithographic inks include high viscosity, good flow and transfer properties, good tack values for sharp imaging, low misting values, insolubility in water but stable emulsion formation with water and sufficient color strength to reproduce the image at 1-2 micron film thickness.

As in the case of UV-curable flexographic inks, commercial off-set inks require the use of about 10-12% of a traditional photoinitiator package consisting of benzophenone, amine synergist and ITX. The lithographic inks based on this new self-initiating resin technology can UV-cure at commercial line speeds to give prints with good color strength at significantly lower photoinitiator levels. The behavior of these inks on a hydroscope was very similar to that of commercial inks with good viscosity, tack and torque values. A typical lithographic ink formulation is represented in Table 6.

Table 6: Typical lithographic ink formulation

Description	Parts (w/w)
30% pigment dispersion w/ FlexCure™ D30 self-initiating resin	50.0
FlexCure L110 self-initiating resin	46.0
photoinitiator package	4.0

As in the previous examples, the lithographic inks based on the new technology were benchmarked against commercial inks, making particular effort to replace only the oligomer and monomer portions of the benchmark formulations. Pigment Yellow 14 Irgalite LB1W (CIBA), Pigment Blue 15:3 Hostaperm blue B2GD (Clariant) and Pigment Red 57:1 Permanent Rubine L7B01 (Clariant) were the pigments selected for this study. Comparative evaluations of the lithographic ink formulations are listed in Table 7.

Table 7: Comparative evaluation of lithographic ink formulations

Formulation	Pigment (% by weight)	% PI	Dosage to tack-free cure (mJ/cm^2)	60º Gloss	Adhesion (coated paper)
Ashland self-initiating resin	15 (Yellow)	5	<250	35.0	5B
Competitive Benchmark	15 (Yellow)	8	<250	53.2	5B
Ashland self-initiating resin	15 (Red)	5	<250	44.4	5B
Competitive Benchmark	15 (Red)	8	<250	53.6	5B
Ashland self-initiating resin	15 (Blue)	5	<250	50.8	5B
Competitive Benchmark	15 (Blue)	8	<250	53.4	5B

An obvious advantage of ink formulations, based on resins built with the new technology is the lower photoinitiator requirement of the former to achieve comparable adhesion.

Over-Print Varnish

Conventional inks which are oil or water-based, have very poor gloss on more absorbent paper substrates due to the penetration of the liquid components into the paper. It is well-known that un-pigmented UV and EB curable coatings give outstanding high gloss finishes. Hence they are increasingly used both to embellish the look and feel of the conventional prints, and to provide a protective layer. Higher quality coatings may give improved rub and scuff resistance and lower coefficients of friction, on high speed packing lines for example. Specific product resistance such as water, solvent or other chemical resistance can be provided for use in more demanding environments. Varnishes are also used to improve the appearance of UV inks which are often characterized by poor pigment wetting and dispersion. Typical starting point formulations contain up to 10 parts per hundred of a traditional photoinitiator package. A typical OPV formulation based on our technology is represented in Table 8.

Table 8: Typical OPV formulation

Description	Parts (w/w)
FlexCure™ OPV120 self-initiating resin	60.0
reactive diluent	36.0
photoinitiator package	2.0
reactive foam control agent	2.0

A number of low viscosity resins have been developed that can function as an OPV when applied neat without any reactive diluent or additional photoinitiator. The experimental OPV formulations and their properties are listed in Table 9.

Table 9: Evaluation of OPV formulations

Formulation	% PI	Viscosity, cP @ 30^0C	Dosage for tack-free cure (mJ/cm^2)	Gloss (60°)	Adhesion (coated paper)
Competitive Benchmark	10.0	185	<200	95.4	5B
OPV-102003-02	2.0	237	<200	90.1	5B
OPV-120903-07	1.0	174	<200	92.4	5B
OPV-010204-03	0.0	216	<200	90.5	5B
OPV-010804-02	0.0	375	<200	94.9	5B

The examples in the above table demonstrate the performance of various OPV formulated with FlexCure self-initiating resins. An obvious advantage of OPV formulations, based on resins built with Ashland Michael resin technology, over the commercial standards is the no or lower photoinitiator requirement of the former to achieve comparable gloss and adhesion levels. This could be especially advantageous in applications such as food-packaging which mandate no or very, very low levels of extractables.

Summary

In summary, a new resin technology has been introduced that offers unique self-initiating cure upon UV irradiation. This unique photo-reactivity and associated reduction of required photoinitiator may allow UV-curable resin technology to move into additional application areas which are not currently serviced by UV technology. Structural variations within this resin family are limited only by the number of acrylate monomers and oligomers and the number of β-dicarbonyl compounds available.

Resins have been customized for excellent pigment wetting characteristics and can be designed to function as a single dispersions or let-down vehicles for different pigments in various ink applications such as screen, flexographic, and lithographic printing. Dispersions prepared using this new resin technology offer lower viscosities at equal pigment loading or the potential for significant increases in pigment loading. Ink formulations based on these resins show excellent printability characteristics and a lower photoinitiator requirement to achieve better gloss and comparable adhesion levels at lower formulation viscosities. OPV formulations containing no or very low additional photoinitiators have been developed which show comparable gloss and adhesion performance to commercial OPVs and could be very useful in food packaging and other related applications.

References

1. T. Moy, L. Dammann, R. Loza, US Patent 5,945,489 (1999)
2. T. Moy, L. Dammann, R. Loza, US Patent 6,025,410 (2000)
3. M.Sheridan, T.Moy, M.Gould, S.Narayan-Sarathy, T.Marino, A.Mejiritski, D.Martin, RadTech 2002, Technical Conference Proceedings, p. 462-474.