Energy-curable inks and coatings have been an active field of research and development for more than 30 years. A growing marketplace acceptance of traditional energy-curable materials suggests a compelling value proposition for such products. At the same time, advancements in industrial inkjet technology have been occurring at a steady pace for almost as long, allowing industrial inkjet processes to play a major role in the emerging digital printing market.

A marriage between the respective value propositions for energy-curable and inkjet technology is exciting from both commercial and technical standpoints. By way of introduction to UV-inkjet ink, a general discussion of each of the main components of the UV-inkjet technology value delivery system is given. This is followed by a review of the state of the art of UV-curable inkjet material compositions with a particular emphasis on recent advancements in UV-inkjet ink formulations.

**Introduction**

The respective value propositions associated with traditional energy-curable inks/coatings and inkjet technologies are compelling in their own right. It is well known that energy-curable inks and coatings provide valuable emissions control advantages but the real market drivers are improved product performance and increased production efficiency.1,2 Specifically, traditional energy-curable (e.g. UV, EB) systems provide increased energy savings, faster production rates and floor space savings. In addition, low-odor/low-extractable materials, zero volatile organic content (VOC) and virtually zero hazardous air pollutants (HAPs) are key advantages. On the other hand, industrial inkjet systems may also improve production efficiency. Decreased setup and switch over times as well as decreased consumables waste are enjoyed by inkjet end-users. Further advantages may include lower inventory levels, short run efficiency and shorter lead times. Variable information printing on a wide range of substrates and an overall decreased cost are also among the key market drivers for this type of printing process.2 Given their respective advantages, it is easy to understand the growing level of marketplace acceptance of both traditional energy-curable materials and industrial inkjet printing.

It stands to reason that a marriage of these two value propositions results in a multitude of commercial advantages for UV-inkjet systems.

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UV-inkjet systems. Recently, Stowe, Caiger and Fuchs described the benefits and key market drivers for UV-inkjet systems in three separate papers.\(^{4,5,6}\) They suggested that the potential benefits specific to UV inkjet may be zero solvents/VOCs, which facilitates long nozzle open times, hence greater jetting reliability. The life expectancy of the inkjet print head is increased because there is no drying or clogging in nozzles associated with the use of UV-cure inks. Compared to jetting solvent-based formulations, UV inks offer significant head reliability and performance in this area. Instantaneous drying upon exposure to UV radiation as opposed to water or solvent evaporation increases production efficiency. They also suggested that improved opacity and decreased dot gain resulted in improved print quality. At the same time, final prints exhibited increased weatherability, scratch and chemical resistance and decreased odor and taint. It shouldn’t be surprising that a growing number of inkjet machine manufacturers and the requisite value/supply chain are starting to adopt UV-inkjet processes.\(^{7}\) Moreover, a case analysis was recently published by Dave King in which he described how one shop justified the purchase of a UV flatbed inkjet machine.\(^{8}\) King’s bottom line suggested that one must consider the advantages and disadvantages of all of the components of the value delivery system while pondering the decision to adopt UV inkjet. Each of the major components in the UV-inkjet value chain is described from the perspective of an inkjet ink manufacturer.

**UV-Inkjet Ink Value Delivery System**

The UV-inkjet ink value chain (see Figure 1) from the perspective of an inkjet manufacturer is similar to the traditional/conventional ink value chain with a few subtle, but extremely important differences. For instance, new developments along this value chain tend to happen because of strong interactions between the various participants in the value chain. In other words, integrated approaches toward technical challenges have advanced UV-inkjet technology in recent times. Unlike traditional printing processes, it is absolutely critical that the major machine components such as the print heads and the UV source match the inkjet ink and vice versa. Therefore, there are technological constraints, namely materials compatibility, viscosity and surface tension requirements, on the composition and properties of the ink that must be addressed at the time of formulation. Not only does the cured ink have to have good mechanical/physical properties and exhibit good print quality, but it also must jet reliably and be compatible with the machine component materials.

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**Figure 1**

*Inkjet value chain from an inkjet ink manufacturer’s perspective*

![Inkjet value chain diagram](image-url)
Unlike traditional UV-ink and coating formulators, UV-inkjet ink makers require specialized materials given the unique set of technological constraints of the inkjet printing process. Suppliers of monomers and oligomers for traditional inks and coatings recognized the UV-inkjet opportunity. For example, Klang and Balcerski discussed the monomer/oligomer supplier role in the emergence of UV-inkjet technology. They suggested that, typically, most film forming materials exhibited a viscosity much higher than that required for good jetting. They also suggested that oxygen inhibition, rapid curing, health and safety as well as cost were also important criteria for developing new materials for UV-inkjet applications. They introduced a new family of polyester acrylate oligomers for use by UV-inkjet formulators in 100% UV systems. These new materials reportedly exhibited an inkjet friendly viscosity vs. temperature profile as well as relatively low shrinkage upon curing. In another instance, Rijoy Putatunda discussed UV-inkjet vehicles in May 2002. These products, marketed under the trade names Viajet 100™ (100% solids grinding) and Viajet 400™ (letdown vehicle), are now commercially available for UV-inkjet applications. It was reported that low-viscosity inks with low odor, low color, and excellent jettability could be obtained from these products. In both cases, UV inkjet was cited as the newest and fastest growing segment in the energy-curing materials technology space. It is almost certain that we will soon see further advancements in oligomer technology. Astute companies will see the growing need for specialty UV monomer/oligomers and join the UV-inkjet value chain in the near future.

**Pigments**

Pigment and pigment dispersion suppliers have long recognized the need for special inkjet materials. Pigments have been produced for the inkjet market with ultra fine average particle sizes and narrow particles size distributions \( (D_{avg}<500\text{nm}, \text{none above } 1000\text{nm}) \) for quite some time. However, novel pigment dispersions for UV-inkjet inks were recently related by Herrmann et al. in U.S. patent 6294592. In this case, small particle-sized pigments were combined with a UV-curable binder, dispersant and water to obtain dispersions useful in water-based UV-inkjet applications. Dougherty et al. recently described pigment dispersions for both 100% UV inkjet and UV-curable, water-based systems. They discussed the use of UV-curable polyester acrylate oligomers in combination with hyperdispersants as pigment dispersing agents in generating low-viscosity, stable dispersions suitable for UV-inkjet ink formulation. Dougherty also described a novel UV-curable cationic dispersant for use in waterborne formulations. The new dispersant contributed to increased hydrolytic stability of waterborne inkjet ink formulations. UV-curable dispersions appear to be a relatively new link in the UV-inkjet ink value delivery system and their potential advantages are not lost on UV-inkjet ink manufacturers.

**Photoinitiators**

Photoinitiators (PIs) are key components to any UV system including UV-inkjet ink compositions. Given the aforementioned low viscosity constraint for these types of systems, oxygen inhibition becomes an even greater concern with respect to curing efficiency. Andre Fuchs et al. recently discussed the importance of optimizing the PI-pigment balance in low-viscosity UV systems. He suggested that a novel, efficient difunctional alpha hydroxyketone could be used to overcome the increased oxygen inhibition in model UV-inkjet systems without adversely affecting colloidal stability. Good curing efficiency is required to minimize migratables, which may include unreacted monomer. Caiger and Herlihy discussed the role of PIs in UV-inkjet food packaging application. They suggested that a poor cure of ink films could lead to the migration of unreacted monomer. However, odor and taint problems in food packaging are more likely caused by the photoinitiator and/or its fragments. Caiger and Herlihy demonstrated the use of efficient multifunctional photoinitiators (MFPIs), where several PI groups are attached to a core molecule. Once reacted, the MFPI is then bound by the resulting polymeric film rendering it immobile. Another approach to achieving low odor and taint is minimizing the amount of PI. Deckers showed that useful compositions could be generated with only very small amounts of PI. Unique PI development for UV-inkjet systems remains an important area of consideration in the development of commercial UV-inkjet applications.

**UV Sources**

Activating the PIs and curing the pigmented ink as it jets onto various substrates at various film thicknesses using various machines is not a trivial matter. The physical properties of the ink film can be greatly affected by the cure. Stowe recently reviewed UV-source technology and suggested that spectral distribution, peak irradiance, total UV energy and IR/heat radiation control are the four main variables to consider when developing a machine and/or an inkjet ink. A key integration issue for OEMs is the proximity in which the UV source is placed with respect to the jetting assemblies. Stray UV radiation can cause nozzle failure and must be avoided. A growing number of choices for UV sources are
available, allowing OEMs greater flexibility in their machine design including the use of light emitting diodes (LED). Stephen Siegel recently described the emergence of UV LED array technology which emits virtually no IR radiation and has a relatively long lamp life time. LEDs are also light weight, scalable and reasonably priced. On the other hand, the spectral distribution remains narrow at relatively long wavelengths and the total UV energy is relatively low. In another instance, flash-curing systems have been reported in the literature. Smith taught the use of water-based UV-curable inkjet compositions useful with high-energy electronic flash source. The UV-source component of the UV-inkjet value chain is a key area with respect to integration as is the inkjet printhead component.

**Printheads**

In general, more major advancements in the inkjet printing process have been a direct result of advances in the printhead technology. Examples of some of the latest print head technology are shown in Figures 2-4. A review of printhead basics can be found in any number of different sources including articles by Le and Laird. A detailed historical review of printhead technology is beyond the scope this article; however, in the most basic sense, there are two types of printhead technologies namely continuous (CIJ) and drop-on-demand (DOD). In the case of continuous inkjet printing, drops are formed from a continuous stream of ink by applying a pressure wave pattern. These drops pass between electrodes, which induce an electrostatic charge. Charged droplets can then either be deflected from the stream toward a substrate or toward a collection reservoir. The remaining droplets in the stream are collected in said reservoir and re-circulated. On the other hand, DOD technology generates droplets by the mechanical action of a piezoelectric crystal or thermal pulses. In its infancy, inkjet technology was dominated by the continuous inkjet process. In recent times, it has been major advances in DOD technology that have enabled further inkjet ink development. Klang and Balcerski suggested that piezo DOD technology dramatically increased the range of ink viscosity for good jettability. An expansion of the physical property constraints on the jettable fluid allow greater flexibility with respect to the inclusion of higher molecular weight materials and/or increased higher molecular weight fractions. Traditionally, UV-inkjet ink suppliers have developed close partnerships with print head manufacturers in order to ensure the print head components, materials, and adhesives are compatible with UV-cure inks. In some cases, the print heads had to be slightly redesigned or a totally new head developed due to handle UV inks vs. jetting traditional
aqueous-, oil-, and solvent-based inks. Recently, major printhead manufacturers have announced new breakthroughs in precision placements of drops and gray scale printing (variable drop size) thus continuing their technology leadership in the UV-inkjet value delivery system.

OEM

UV-inkjet machine manufacturers integrate the components of the UV-inkjet ink value delivery system. There are as many choices as there are applications. A few examples of industrial UV-inkjet machines are provided in Figures 5 and 6. A review of the machine offerings available is beyond the scope of this paper and the readers are referred to more comprehensive sources including the article “Large Format Report: Nothing But Net...Profits,” which appeared in Digital Output magazine in July 2003 as well as “Flat-out Getting to the Profits,” which appeared in Digital Graphics in October 2003. The authors refer those readers not well versed in the art of inkjet printing to this solid review. In his paper, Le predicted the successful development of economically and technologically sound UV-inkjet inks, but did not review the state of the art with respect to UV-inkjet ink technology. A non-comprehensive but detailed review of UV-inkjet ink evolution follows.

Continuous inkjet machines flourished initially; therefore, initial inkjet compositions were optimized for these types of systems. One of the first known instances of UV-inkjet inks was related by U.S. patent 4228438 granted remain hot topics for researchers. Advancements in UV-inkjet ink technology are reviewed below.

**UV-Inkjet Ink Technology Evolution**

The field of UV-curable inkjet inks has been an active area of research and development for over twenty years. Hue P. Le reviewed inkjet technology beginning from Lord Raleigh’s description of the break up mechanism of liquid streams in 1878 to inkjet technology circa 1997. The authors refer those readers not well versed in the art of inkjet printing to this solid review. In his paper, Le predicted the successful development of economically and technologically...
to H. Vazirani of Bell Laboratories in 1980. Vazirani described the use of energy-curable materials in a continuous inkjet printing system used for marking cable sheathing. In order to maintain high-printing speeds and good adhesion while obtaining high-contrast printing on irregular surfaces, Vazirani invented a unique ink system that comprised a radiation-curable prepolymer dissolved in solvent. The prepolymer was described as either an epoxy acrylate or a urethane acrylate. Pigments such as TiO₂, small amounts of ammonia and other additives were dispersed in this solution to yield an energy-curable inkjet ink suitable for a continuous inkjet process. In this case, polar solvents remained a major part of the ink formulation by weight. At approximately the same time, A. Young and the Mead Corporation related the use of radiation-curable ink compositions in U.S. patent 4303924 in part to circumvent the disadvantages of using water. Young taught the use of various multifunctional ethylenically unsaturated acrylate moieties in conjunction with a reactive synergist and with and without an ultraviolet photoinitiator. These types of formulations were useful for continuous inkjet machines and could be exposed to UV or electron beam radiation to yield a cured printed pattern. Young also preferred to use organic polar solvents in the ink formulations. In 1983, D. Maxwell of the American Can Company described an epoxy-based energy-curable system, which also used solvents to control viscosity. Unlike Vazirani, Maxwell did not use any ethylenically unsaturated moieties. Instead, she used cationic photoinitiators as opposed to free radical generators to polymerize the epoxy components. Maxwell’s ink compositions were also useful in continuous inkjet machines. Bruce Lent and Nikolay Shevelev also used organic carriers in their formulations for inkjet printing etch resists in the manufacturing of circuit boards. Lent and Shevelev also taught the use of a combination of multifunctional acrylate materials and epoxy acrylate resins. They suggested that the proper balance of adhesion and removability could be obtained by incorporating a certain level of carboxyl functionality in the materials that made up their ink formulations. Over the course of the 1980s and early 1990s, the three main types of UV-continuous inkjet compositions were established namely free radical, epoxy and combinations of both of these.

It wasn’t until 1990, that energy-curable compositions were reportedly jetted with thermal head technology. C.K. Chieng, of Hewlett Packard, recognized the disadvantages of thermal-based drying methods for printed plastic parts. He taught the use of HP’s thermal head technology with UV-curable formulations, which were useful for printing on plastic parts such as computer and electronic components. Chieng described a three-component system that comprised a commercially available energy-curable adhesive, dye and solvent/diluent system suitable for use with but not limited to thermal heads. Interestingly enough, water in combination with organic solvents was exemplified in this particular patent. Previous researchers sought the elimination of the water component and all of its disadvantages as key to achieving reliable continuous ink jet printing although a strong reliance on volatile organic solvents remained. Water-based and solvent-based UV-inkjet inks have their respective places in the industry since good print quality is dependent, in part, on the substrate. Murray Figov suggested that UV-curable, water-based formulations can be used when printing on substrates that have some water absorbency (i.e., paper, cardboard). Figov related a solution to both the drawbacks associated with the use of solvent components (i.e., strike-thru and environmental, health and safety hazards) and those associated with water (water fastness and finger smudges) could be eliminated using UV-curable, water-miscible components along with a colorant and possibly a bridging fluid. In 1994, Allan Marshall and Allan Hudd related an ink composition that was free of volatile organic compounds. Marshall and Hudd suggested that for a continuous inkjet process, as long as the water-soluble conductive compound was chosen such that it was soluble in the ethylenically unsaturated components then there was no need for the organic solvents. This also eliminated the possible disadvantage of ink drying in the nozzle of the print head.

Even though 100% solids UV-inkjet formulations do not have the drawback of drying and clogging nozzles, they are not without their disadvantages. A number of ethylenically unsaturated materials well suited for use in UV-inkjet systems are also under scrutiny for having relatively high irritancy. Caiger and Selman addressed this issue and developed novel UV-inkjet formulations which incorporated alkoxylated and/or polyalkoxylated ethylenically unsaturated materials into UV-inkjet inks. These particular materials exhibited relatively low irritancy while maintaining good jetting and curing properties. Another technical challenge of low-viscosity UV-inkjet formulations is the control of drop spread. Caiger and Selman also developed UV-curable, hot melt inkjet ink formulations where the material was quite viscous at room temperatures, but exhibited relatively low viscosity at increased jetting temperatures. Upon coming into contact with the substrate the droplet...
would phase change, hence limiting the amount of spread before curing. These formulations did not suffer from the same lack of durability as traditional hot melt inks.

More recent advancements in UV-inkjet ink technology exemplify the importance of maintaining low viscosity while generating useful final print properties. Vanmaele related novel low-viscosity inkjet compositions comprising novel radiation-curable monomers that were characterized by both vinyl ether and acrylate functionality.33 Ylitalo et al. discovered that low surface tension solvents used at certain levels in UV-curable inkjet ink compositions acted as a flow agents as well as a diluents thereby providing a wider latitude for incorporating higher molecular weight materials, which in turn exhibit robust physical properties when cured.31 She also suggested that the vapors generated during the curing reaction may also act as a barrier to oxygen inhibition. Carlson et al. demonstrated the use of a new polyester urethane oligomer.34 They found that a radiation-curable polyester oligomer could be incorporated into low-viscosity, UV-inkjet compositions without further dilution with non-reactive solvents. Novel solutions to the fundamental challenge of formulating jettable fluids while achieving robust final properties will continue as UV-inkjet ink technology continues to evolve.

Summary

The UV-inkjet value delivery system delivers a number of key benefits not the least of which is increased production efficiency with similar print quality. On the other hand, there remains a continuous demand for improving production efficiency, reliability and line speed of UV-inkjet printing processes. Therefore, a tremendous amount of pressure is placed on the developers of UV-inkjet ink technology by the OEMs and end-users in the value chain. The result of this pressure is apparent from the numerous advancements found in the technical literature. OEMs, printhead manufacturers and UV-inkjet ink manufacturers continue to develop larger designs, which will offer a wider print area for future commercial graphics, industrial marking and packaging applications. It is these markets that will drive the future success of UV inkjet. Fortunately, a strong integrative approach has been adopted, which will facilitate further refinement and evolution of UV-inkjet ink technology in the future.

References

11. Product literature from Clariant, Ciba and Cabot-SMP.

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