# Printing with Energy-Curable Inks—
# High Energy Chemistry, High Energy Business

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Keywords: Electron, Beam, Radiation, Cure, Photopolymerization

Abstract: Inks that can be instantaneously cured on press through exposure to Ultraviolet (UV) or Electron Beam (EB) energy are widely used in lithographic, flexographic, screen, letterpress and ink jet inks, as well as an array of clear top-coats for print. The key technology factors in UV/EB ink curing and formulation will be discussed, as well as the impact of this chemistry on the different printing processes. Both the operational issues and the print performance issues that are driving growth in this area will be covered. Issues of UV vs. EB, as well as issues of energy curable vs. conventional inks, will be included.

## Introduction

My colleagues and I are going to introduce what will be, for some of you, a new technology. This technology has been commercial in the graphic arts industry for at least 30 years, and the underlying technical principles have been known for much longer than that. In the last decade, however, there has been an explosive growth in the use of energy curing technology by printers, and we felt that a technology summary session here at TAGA would be appropriate.

I am going to address four questions:

What is the Energy Curing process?
How do Energy-Curable products compare with conventional ones?
How are these products formulated?
What are the pressroom issues seen with Energy-Curable products?

## What Is Energy Curing?

For graphic arts, Energy Curing means the printing of chemically reactive inks or coatings followed by in-line exposure of the print at normal press speed to an energy source that will essentially instantaneously cause the curing, drying or

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photopolymerization of the ink and coating, leaving a fully dry, ready-to-ship product as it comes off the press. In more than 99% of commercial installations, the energy source is either an ultraviolet bulb or an electron beam.

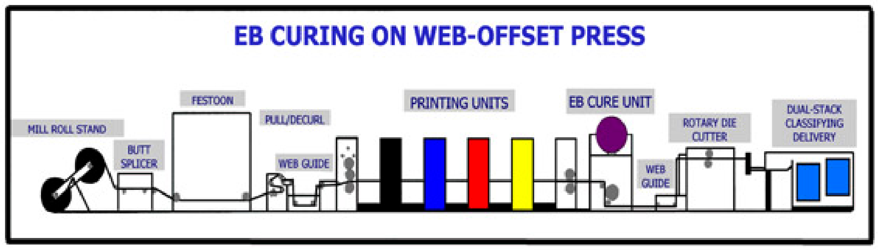


Figure 1. Energy Curing follows standard printing in-line at press speed.

Energy Curing printing can be done with most printing processes, including lithography, flexography, letterpress, screen, gravure and ink jet. The largest volume applications are litho, flexo and screen, and the fastest growing applications are flexo and ink jet. All of these are done with UV curing, and web litho printing also is done EB. There is a lot of activity around EB flexo for CI presses, and I expect to see some commercial installations this year.

Almost every kind of print application, except publication printing, is being done with Energy Curing somewhere. The largest area is food packaging, but many types of product packaging, labels and commercial print are done with UV or EB.

In the United States alone, there are thousands of UV installations and dozens of EB installations just for graphic arts. The technology is also widely used in the adhesives, wood coating and automotive industries. There are several suppliers of all types of UV/EB inks and coatings, of UV lamps and of needed equipment and supplies. There is one dominant and one small U.S. supplier of EB-curing equipment for printing.

To complete the definition of Energy Curing, we need to look at four more topics:

How does it work, chemically?
How does it work, mechanically?
Where is it used?
Why is it used?

**Chemically**, energy curable inks and coatings are made up of many standard ingredients, like pigments, waxes and defoamers. However, the predominant part of the formula consists of a mixture of materials all having pendant, reactive acrylate functionality. When this mixture of materials is exposed to a suitable energy source, the acrylate double bonds polymerize and cross-link, forming a tough, 3-dimensional polymer network on the print substrate.

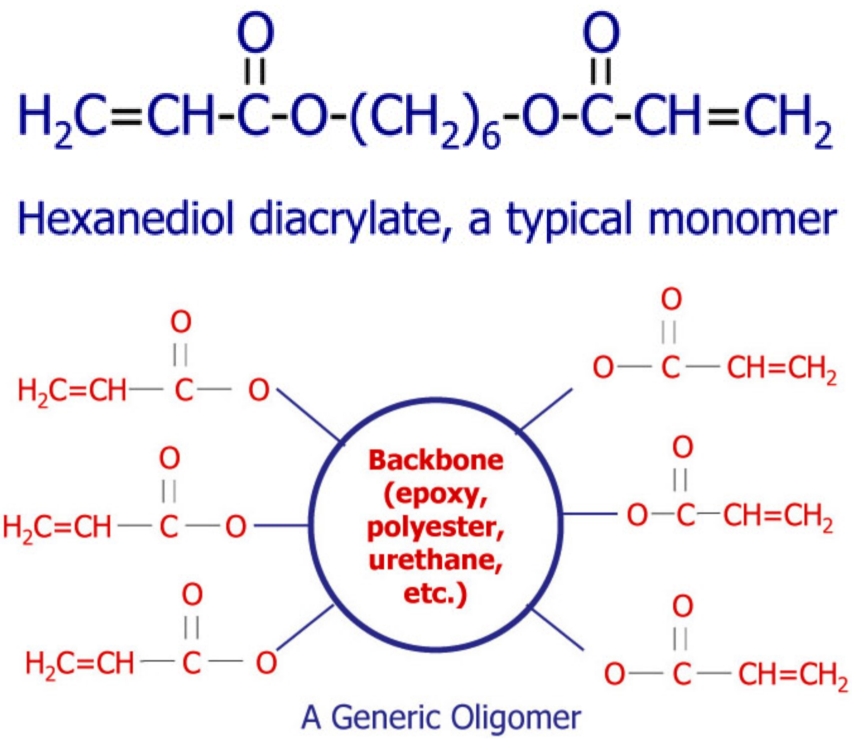


Figure 2. A typical monomer and a generic oligomer.

These curable materials fall into two classes, loosely based on molecular weight. Lower molecular weight materials, usually less than 1,000 daltons, are usually known as monomers. These tend to be fluid and fill the role of an ink oil in a conventional litho ink, or of the water or solvent in a fluid flexo or gravure ink. Since these monomers are reactive, they can be fluid carriers and yet be incorporated into the cured ink film without worrying about forced evaporation or absorption. Monomers will often have between one and four reactive acrylic groups, although some have higher functionality.

The second class of curable materials has higher molecular weights, often from 1,000 to several thousand daltons. This is not large enough to meet most people's definition of a polymer, and thus they are known as oligomers or prepolymers. Oligomers are conceptually made from a polyol backbone of some other technology, such as an epoxy, a polyester, a urethane or some other chemistry, that is then esterified with acrylic acid to make the resulting multifunctional curable oligomer. In practice, many of these products are made almost *in situ*.

Most of the performance properties of the ink come from the oligomers. Before curing, the oligomers are largely responsible for lithographic performance, ink/water balance and dot gain for litho printing, and they are responsible for issues like pigment dispersion, flow and dot gain in flexo printing. During curing, oligomer selection significantly affects cure speed. After curing, issues like chemical resistance, rub resistance, gloss and coefficient of friction are affected by the oligomer.

One other critical concept is the essential difference between UV-curable and EB-curable products. A curtain of high-energy electrons falling on a thin film of energy-curable ink or coating has enough energy to begin and complete the curing process without any help. The energy output from a UV lamp, however, is much less. Thus, UV-curable inks require a photoinitiator, which is a chemical that can accept the UV energy from the bulb, decompose, and have its high-energy decomposition fragments pass the energy to the curable components of the ink or coating. Photoinitiators are designed to have a chemical structure that absorbs energy at the peak emission wavelength of the UV bulb, and also to have a labile bond that will undergo homolytic cleavage to create relatively stable free radicals. These free radicals initiate the curing process.

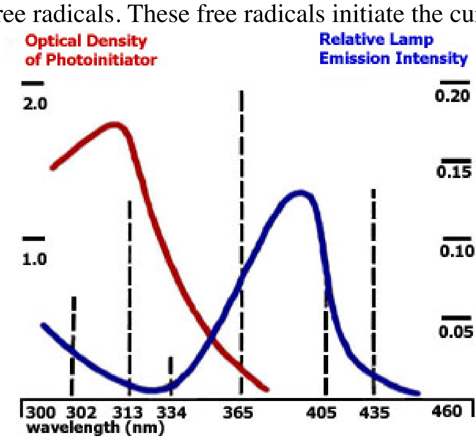


Figure 3. Photoinitiator absorption matches UV lamp emission.

**Mechanically**, there are many similarities and some differences with conventional printing. For now, let's just look at the issues with lithography and flexography.

In sheetfed litho, the curing process will be UV only. This is because of some EB limitations that we'll discuss later. There are still, however, two major options. The first option is to use so-called conventional UV inks. These are UV-curable inks that are designed to be cured by exposure to UV energy *after each printing unit*. Thus, the inks are dry-trapped. The second option is to use the so-called UV hybrid inks, which are designed to print and cure with one UV station after the last printing unit. These inks are wet-trapped.

Differences also exist in the ink formulas depending on whether the print substrate is paper-based or a non-absorbent plastic or foil. The paper vs. plastic mechanical issues are largely the same as they are for conventional oil-based litho inks.

Clearly, there are some formulation differences between conventional UV and UV hybrid inks. From the mechanical perspective, there are three main issues:

rubber composition of rollers and blankets,
location and spacing of UV lamps and
UV coatability.

Some fluid monomers used in conventional UV inks are quite aggressive. Normally, EPDM rubber is used in rollers and blankets for presses that only run UV. EPDM shows good resistance to swelling and excellent compatibility with UV ink systems. UV hybrid inks, however, are designed to run on the Buna-N rubber used in most presses running oil-based inks. There are some performance sacrifices made in switching to non-swelling ink components, and different ink makers have different strategies for this. However, most people have found that the convenience in being able to switch back-and-forth between oil-based and UV hybrid inks on the same press is a strong advantage. Still, for a committed UV press, EPDM is the best choice.

Lamp location is a critical issue. Most conventional UV printers use interstation curing, wherein a UV curing lamp is mounted after each printing unit. This dry-trapping mentality eliminates concerns about tack rotation and color contamination in the later printing units. Also, the printed dot is frozen by the curing process only milliseconds after printing, which can offer some dot gain advantages.

With UV hybrids, some printers use just one curing unit that is placed after the last printing station and before the coater. This creates a 100% wet-trapping situation, with all the issues that exist in oil-based inks. Other printers will install two or three portable curing units, with one of them still at the end of the press. This allows some flexibility if, for example, the printer wants to use a first-down white. With multiple UV lamps, a printer can cure the white, or even double-bump and cure the white, and then wet-trap colors over the dry white. In other cases, especially with dark colors or metallics, it may make sense to cure the inks before trapping on them.

The primary reason that UV hybrid inks exist is because of UV coatings. Printers of oil-based sheetfed inks have always wanted the 90+ gloss that is routine with UV coatings, rather than the 60s-70s gloss obtained with water-based coatings. Since the UV coating is applied and fully cured while the underlying oil-based ink is still wet, there is surface buckling that takes place as the ink dries. The result of printing UV coating directly on oil-based ink is normally 20-40 points of gloss reduction over a day or two as the ink dries. This is an unacceptable situation. The initial remedy was to use a double coater, and place an intervening layer of water-based primer on the ink, and then UV coat on top. This process gives good gloss, but is expensive in hardware and in the water-based primer. UV hybrids were designed to run on conventional rubber rollers, to cure in-line with one unit at the end of the press, and *to UV coat without glossback.*

For litho web printing, either UV or EB curing may be used. The issues for UV are essentially the same as for sheetfed. Since web presses will be committed to Energy Curing printing, they will normally have only EPDM rollers. The EB issues revolve around the EB curing unit being a large, expensive device that can only be used at the end of the press. This means that the inks are wet-trapped, and that tack rotation and all other wet-trapping issues are involved. Also, EB curing must be done in an oxygen-free, nitrogen-purged zone. This means that the EB curing device has narrow slits for the web to enter and exit, in order to minimize nitrogen loss. This is what limits EB to web processing, because slits big enough to admit sheetfed gripper bars allow a financially unacceptable amount of nitrogen leakage.

Energy cure flexo printing is historically UV only. Since flexo is designed to be a dry-trapping process, UV-only with full interstation curing is the rule. And, for in-line presses, this is a firm limitation. Since flexo is a typically web process, EB seemed a possibility. The problem is the EB cure unit at the end of the press, requiring wet-trapping. This can’t be done with in-line presses because they have top-side turn bars that will smear the wet ink.  CI presses, however, do not normally have top-side turn bars. There has been much work, and some published R&D and trial successes, on EB curable flexo inks that can wet-trap but still have enough flow to transfer with high-line aniloxes on CI presses.

**Where is it used**? To date, EB litho printing is mainly for food packaging. UV litho printing is used mainly for various types of retail folding cartons, commercial printing, forms, metal cans and food packaging folding cartons. EB litho printing makes up around 20% of the EC litho market and is, to date, 100% on web presses and around 90% for food packaging. Nearly all EB food packaging printing is on either a board (SBS, CCN) or on polyboard. Most of the rest of the EB litho market is for labels that have a high need for chemical resistance.

UV litho printing makes up about 80% of the EC litho market. The sheetfed-to-web ratio is about 1:1. Sheetfed UV litho can be for folding carton, commercial printing, forms, advertising, metal cans and many sub-markets. Substrates used vary from uncoated forms paper to board to coated commercial stock to many plastics, vinyls, films and foils. Web UV litho printing is mostly for food packaging on board or polyboard. UV litho printing for metal beverage cans is a large market, but requires specialized presses.

The three big markets for UV flexo printing are tags and labels, folding cartons and flexible packaging. UV flexo folding carton printing is a rapidly growing area. Most of the business is in either personal care products or in other consumer goods.

**Why is it used**? UV litho, EB litho and UV flexo have some features in common that encourage their use, but there are also individual advantages for each area. The common feature is high quality print with a high degree of product resistance and moisture resistance that are cured in-line and are ready to die-cut, ship and use immediately as they come off the press. This is an enormous advantage vs. conventional oil-based litho printing, since pallets of work-in-process sitting around and drying are no longer required. Also, the ability to meet short lead-time requirements is dramatically increased.

EB litho offers some advantages over UV litho in that the degree of cure that is achieved is higher. There are no good, quantitative measures for degree of cure. However, it is known that the energy input of the EB unit is higher than a UV unit, and it is known that EB print has no residual photoinitiator fragments in the ink film, and it is known that EB print has a lower degree of residual extractables and volatiles in the cured ink film than UV does. These factors together encourage people to use EB preferentially to UV for food packaging.

Lest I mislead, UV litho printing is fully satisfactory for food packaging and it is widely used in Europe and is well known in the U.S. Also, for short print runs, EB is a less economical option due to its limitation to web printing. However, since test results show that EB residuals in the ink film are even lower than the very low levels from UV printing, EB is more common for longer run food-packaging work. From both processes, given optimal curing conditions, the total residuals in a cured ink film as measured by a purge-and-trap, GC/MS method are usually less than 100 ppm.
Two other important reasons are the green, environmentally friendly nature of UV and EB inks, especially relative to low VOC content and low residuals in the cured film, and their broad adhesion properties to a wide range of plastic substrates.

## Comparison with Conventional Inks

One difference between energy-curable inks and conventional inks is the odor. This is true regardless of what “conventional” means. All energy curing inks and coatings have an odor that, while fairly low in quantity, is quite different in quality from oil-based, water-based or solvent-based products.

A second difference that is universal is the stay-open nature of energy-curable inks. They will remain wet until exposed to an energy source sufficient to initiate curing. Energy curable inks spread out on a lab bench can remain wet and fluid indefinitely. Oil-based inks will oxidize and dry, and conventional fluid inks will dry through evaporation, but energy curing inks will remain wet until you cure them. This removes many drying-on-the-press problems seen with conventional inks, but it also increases their potential to be tracked around and makes housekeeping even more important.

A third difference is that energy-curable products, in their wet state, are skin irritants. Uncured monomers and oligomers left on the skin will, over time, cause a rash resembling a sunburn. This is easily handled by washing with soap and water after exposure, but even better handled by the proper use of personal protective equipment and good housekeeping methods.

A fourth common difference is that energy-curable products are more sensitive to storage and handling conditions. They must be stored in climate-controlled areas, so as not to exceed 90°F, or 32°C. They should not be left out on a loading dock sitting in the sun. They should not be exposed to light sources having a UV component, such as fluorescent lighting, for extended periods of time. And, they should never be exposed to active metals, such as iron or copper. Any of these situations causes the generation of free radicals in the ink and can cause premature curing, or at the very least, can shorten shelf life. Even with cautious handling, EC inks will have a shorter shelf life than conventional inks. Most EC inks will be fine for six months or so if handled properly, but many conventional inks will last several times longer than that.

A fifth area is the oxygen-inhibition effect. Oxygen will slow or prevent the curing of UV and EB inks and coatings. For oil-based inks, oxygen is required for drying to occur. For water-based and solvent-based inks, evaporation is the key issue and oxygen levels really don't matter. The oxygen inhibition effect in energy-curable products shows up in several ways: 1) energy-curable inks are often packaged in plastic containers that allow a level of "breathing," thus extending shelf life, 2) when premature curing in the container occurs, in begins in the center and gradually expands to the outside, and 3) nitrogen purging of the cure zone can be beneficial for UV and is required for EB.

Sixth, the curing mechanism itself is quite different. UV inks use UV-emitting bulbs, bearing a physical resemblance to fluorescent bulbs, with some associated hardware, that are often placed on the press after each curing unit. EB printing uses a single large curing unit at the end of the press. Conventional heatset and fluid inks usually have some type of oven where heat and air flow are critical control issues. Most sheetfed presses have no drying hardware at all, unless they have a coating unit.

### Energy Curable Formulation Issues

At the simplest level, energy-curable products are formulated exactly like conventional products. Some type of pigment concentrate, such as a flush, a dry-grind base or a dispersion, is combined with a let-down vehicle and sufficient additives to achieve the desired performance properties. Like everything else, though, the devil is in the details.

**Pigment Concentrate**. As in conventional products, the non-pigment parts of the pigment concentrate must do two things: they must disperse the pigment efficiently and they must be compatible with the rest of the ink ingredients. For UV and EB inks, these fluid and resinous materials must be energy-curable. Unfortunately, energy-curable products are not as effective at pigment dispersal as many of the resin systems used in oil-based, water-based or solvent-based inks. This means that special effort in both formulating and manufacture must be made to make stable pigment concentrates that are competitively strong and that have the right rheology for the application. A successful product line can be built several ways, but it will involve close cooperation among the inkmaker, the monomer/oligomer supplier and the dispersion hardware manufacturer.

**Let-Down Vehicle**. The components of the let-down vehicle are also energy-curable monomers and oligomers. Here, a balance must be struck between cure speed (achieved with high functionality), substrate adhesion (achieved with film flexibility and lower functionality), product resistance (which will define the backbone chemistry of the oligomer), gloss, rub resistance, and other properties. The optimal formulation for one property is often exactly the wrong thing to do to achieve another equally essential property. Finding the local optima among the many formulation options for all these properties is the key.

**Additives**. In addition to the photoinitiators used in UV-curable products, other additives such as waxes, silicones, defoamers, surfactants, flow aids and rheology modifiers are also used, exactly as they are in conventional inks. One difference is that these additives must be compatible with the energy-curable vehicle system. Another difference is in the types of defoamers, since the foam structure is different than that seen in water-based systems. And, of course, no biocides are needed.

## Issues in the Pressroom

In addition to the odor difference and the presence of the UV or EB curing units in the pressroom, there are a couple of other issues in the runability of UV/EB inks and coatings. I will limit this discussion to the two largest volume areas, litho and flexo.

**Lithography**. The primary benefits of EC litho are 1) that it gives very sharp, good quality print, 2) it can be used on a wide variety of substrates, 3) it is a very green, low emission process, 4) very good chemical resistance can be obtained, 5) the curing process is at low temperatures and will not damage temperature-sensitive stocks and 6) the ink is fully dry and ready to ship immediately as it comes off the press.

UV/EB printing is used on a wide variety of substrates, from paper and board to metallized foil, static cling, polyboard, hologram stocks and polystyrene. These inks tend to have broad adhesion properties.

UV and EB litho inks are high-solids, low-VOC inks that will give extremely low emissions and can be an advantage when permitting a new pressroom. Many of these products are essentially zero VOC, although some additives can contribute a VOC content.

Both UV and EB curing are low-temperature processes and can be used with temperature-sensitive plastic stocks. There is more heat generated with UV than with EB, but much work had been done in developing cool-running UV lamps.

The biggest change that litho pressroom personnel will notice in going from oil-based to energy-curable inks is that the ink/water operational window is smaller between scumming and emulsifying. Even with the fountain solutions that are optimized for energy-curable inks, they are more sensitive to variations in fountain solution levels and are not as user-friendly as oil-based inks. This is because the chemical nature of the monomers and oligomers is quite different than the resins and oils in conventional inks. This difference often leads to lower water pick-up numbers for EC litho inks than for oil-based inks.

Another historical difference in EC vs. oil-based litho inks is in their tendency to mist. Oil-based inks use resins that range up to a half a million daltons in molecular weight. This often gives the inks sufficient non-Newtonian rheology to keep misting well under control. The biggest molecules in the EC vehicles are the oligomers, which range up to a few thousand daltons. The molecular weight after curing is extremely high, but during the printing process the low molecular weight oligomers have historically made misting much harder to control. There are some formulating strategies that can minimize misting, but they come at a cost (usually reduced lithographic performance or narrower water window or picking/piling). Also, the chemical nature of curable resins and monomers makes them thin faster as the temperature increases and makes them have a narrower operational window with the fountain solution. Many types of additives and much oligomer process development work has been done, and misting is much less an issue than it was even five years ago. Essentially zero-misting UV and EB products are now available, but they are harder to make and will accept less press-side adjustments than oil-based inks while staying low-misting.

A third litho difference is in tack. UV/EB inks can be any tack they need to be, but they tend to be sold at higher tacks than oil-based inks for the same application. This is partially to reduce misting, but part of the reason is that high-strength inks usually require less water on press (also reducing misting and reducing the potential for emulsification), and that high strength inks give better mileage and sharper dots.

Another area is the proper selection of rubber compounds for rollers and blankets. Some EC monomers act as aggressive solvents, and chemical-resistant rubber is the preferred choice. Some printers will try to run oil-based inks and conventional UV inks on the same press for alternate jobs. This is possible, but somewhat painful. The rubber rollers must go through a conditioning period as the chemistry is switched, and some degree of swell will occur for several hours until the system stabilizes and the stripe can be reset.

**Flexography**. UV flexo inks are higher in viscosity than solvent-based or water-based inks. This enables them to print a very sharp dot. The non-evaporative nature of their chemistry makes the need for press-side viscosity adjustments much less. Also, UV flexo process colors can run at aniloxes well over 1,000 and achieve normal process densities.

One concern is in the compatibility of plates with the UV chemistry. Some plates will experience either slight swell or a change in plate hardness. Balancing the chemistry of the ink with that of the plate is critical. This is done by placing the ink raw material in question on a sample of the plate material, letting it stand for the appropriate amount of time (often several hours) and then measuring both the amount of swell with a micrometer and the change in plate hardness with a durometer.

Another issue rising from the higher viscosity of UV flexo inks is the potential for higher dust pick-up and higher paper waste. The stay-open nature of UV inks together with their higher viscosity (typically 500-1,500 cps) enables them to pick up and retain any airborne particulate matter. This is usually called the "trash" problem. Many UV flexo presses are in enclosed rooms with the feed paper handling and the die-cutting of print taking place outside this room. This will greatly reduce the airborne paper dust issue. In the absence of dust control management, greater print waste can be seen as trash picked up by the ink works its way through the system.

A historical limitation of UV flexo inks has been their poor acceptance on wide-web presses printing on plastic film. This largely due to the heat from the interstation curing lamps causing sufficient expansion of the film that registration is difficult to maintain for high quality printing. There have been successful wide-web flexo trials, and much work is going on in ink companies and in UV lamp companies to fix this problem. It is currently not impossible, it is just too difficult to make a good business today.

One other performance issue with UV flexo is that it tends to be intermediate between water and solvent flexo in the breadth of plastic substrates where there is good ink adhesion. As a result, most UV flexo printing is not on paper or paperboard (where water inks have a cost advantage) nor are they used on low-end plastic bags (where solvent inks have a cost advantage). They tend to be used on narrow-web or mid-web presses printing on expensive plastic or foil substrates in jobs targeting higher print quality.

**Summary**

This 30,000-foot view of the state of UV and EB technologies in the graphic arts areas was designed to inform about a fast-growing area and to spark discussion about what is, and about what could be. There are many resources for more detailed information, including the next speakers and most of the inkmakers in attendance here. The best source for general information about the technology is the RadTech International North America trade association. They are having their biennial technical conference and trade show in Charlotte, NC in two weeks.

I would like to thank the management of Wikoff Color Corporation and the staff at RadTech for their support in preparing this report.