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UV/EB CURING

Primer 1:

- INKS
- COATING
- ADHESIVES

UV/EB CURING PRIMER:

INKS, COATINGS AND ADHESIVES

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ABOUT RADTECH INTERNATIONAL

RadTech International North America, a nonprofit organization, is the association for the advancement of ultraviolet and electron beam (UV/EB) technology. RadTech serves as an industry forum, addressing the educational needs of the users and suppliers of UV and EB equipment and materials.

Since its founding in 1986, RadTech has grown into an organization of well over 800 members encompassing professional experts in the areas of radiation curing equipment and raw and formulated materials technology, and most importantly, users of this fast-growing segment of high efficiency industrial technology.

In order to educate newcomers to UV/EB curing, be they technologists or potential practitioners, a group of RadTech members have pooled their efforts to develop a primer, or first course training manual. This is targeted at applications in which UV/EB curing has seen its broadest acceptance and fastest growth — the use of ultraviolet rays or electron beams with inks, coatings and adhesives. As a primer, this book is intended to give a broad overview of how UV/EB curing equipment operates, what kinds of chemistry and materials formulations work with this equipment, where UV/EB curing has been used in industry and what are some of the health and safety concerns which need to be addressed in using this technology. For the trained engineer and chemist, more advanced texts and articles are recommended.

RadTech's charter is to further UV/EB technology by education. To this end, it sponsors a biennial conference where the latest developments are presented in technical papers. A quarterly newsletter is published updating the activities of the U.S. government as it relates to the industry. The *RadTech Report*, the bimonthly journal of the organization, provides as forum for new technology and business updates. For those desiring a source of suppliers, RadTech also publishes a Buyer's Guide. The *RadTech Test Methods Book* is the single source for methods to test materials. The RadTech Foundation furthers basic research and education.

Throughout the year RadTech sponsors a series of industrially oriented one-day workshops throughout North America in which this UV/EB primer is used as a basic text to teach the fundamentals of ultraviolet and electron beam curing. Information about the dates and location for these workshops can be obtained from RadTech International North America at 708/480-9576. At these workshops or seminars, volunteer RadTech experts review this material and answer specific questions.

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Chapter One

INTRODUCTION: THE NATURE OF ENERGY AND ITS INTERACTION WITH MATTER

HOW IS ENERGY TRANSFERRED?

Nature conveys energy in many ways. Moving air creates wind currents which in turn control weather patterns, sailboats, and kites, and provide cool breezes on warm summer evenings. On a large scale, nature emits electrical discharges in the form of lightning. On a microscopic scale, nerve impulses rely on the flow of electrical charges across the neurons of living animals. Of all the forms of energy found in nature, perhaps none is more prevalent than radiation. Even in the vacuum of space, the moon still receives sunlight. On earth, this same sunlight causes chemical changes to occur in organisms which are essential to the growth of plant and animal life.

We have learned to harness of the energy which nature provides. Forced air systems are used to heat and cool homes, offices and automobiles. Electricity generated at power plants is conducted via low resistance metallic wires to make work easier. At home, resistance to the flow of this electrical energy is used to generate heat in devices such as the heating coils of an electric range. This same resistance is used to heat a thin wire filament which in turn generates light in an incandescent bulb.

In recent years, have learned how to use radiant energy to their benefit. Electron guns of cathode ray tubes emit impulses which activate the phosphor on television screens and computer display screens. Microwaves are used routinely to expedite cooking. Waves of various frequencies are received by antennas and then are electronically converted into sound and pictures. As we close out the 20th century, these more sophisticated uses of energy are becoming more and more commonplace.

Like at home, radiant energy is also finding many new uses in industry. X-rays are not used just for the diagnosis of subsurface conditions in medicine, but also for the analysis of many fabricated materials, such as tires and composites. In converting operations, which historically have used heat energy from forced air convection ovens, ultraviolet and infrared energies are now used in many installations. Direct bombardment of accelerated electrons on specially formulated liquids converts them instantaneously to solids. In addition to the inherent efficiency as a form of energy transfer, radiant energy often also eliminates volatile solvents. These solvents create costs such as the heat needed to evaporate them and the processes required to prevent air pollution.

Unlike nature which for the most part transmits radiant energy in a diffuse, low energy manner, the use of radiant energy by humans to do work must be at a higher energy level. To generate enough energy to run a modest light industrial factory in the sun belt, the most efficient solar reflections would require an estimated 1.5 times the surface area of the factory itself. Clearly, to attain any economic value in using radiant energy it must be intensified as it is generated.

THE ELECTROMAGNETIC SPECTRUM

Radiant energy transfer can be understood from two different perspectives: wave phenomena and subatomic particle movement. All waves, whether the wave motion of the sea or the waves of radiant energy, are characterized by the properties of wavelength, frequency and intensity. The wavelength is the distance between the same portion of two consecutive waves. The frequency is how rapidly the wave recurs, while the intensity is the height of the wave. Radiant energy has been organized based upon the wavelength property to form what is called the electromagnetic spectrum.

Wavelengths in this spectrum range from slightly beyond 10,000 kilometers (10^7 meters) to 10^{-14} meters. All radiant energy in this spectrum has the common property of traveling at 3×10^8 meters/second in space which is the speed of light. There is a well-defined relationship between the wavelength and the frequency, namely:

$$\nu = c/\lambda$$

where ν is the frequency in cycles per second, c is the speed of light and λ is the wavelength. The table below presents the frequencies and wavelengths for the electromagnetic spectrum.

The Electromagnetic Spectrum

Wavelength in meters	Frequency in cycles/s	Type of radiant energy
10^{-14} m	10^{22} Hz	gamma rays
10^{-12} m	10^{20} Hz	gamma and X-rays
10^{-10} m	10^{18} Hz	X-rays
10^{-8} m	10^{16} Hz	ultraviolet
10^{-6} m	10^{14} Hz	visible
10^{-4} m	10^{12} Hz	infrared
10^{-2} m	10^{10} Hz	microwaves
1 m	10^{8} Hz	TV and FM radio
10^{2} m	10^{6} Hz	AM radio
10^{4} m	10^{4} Hz	long radio
10^{2} m	10^{2} Hz	long radio

The third property of wave phenomena, its intensity, is related to the total amount of energy transferred from a source. Intensity is most commonly expressed as wattage. For example, incandescent lights will usually emit light of the same frequency and wavelength for a given type of bulb. It is, however, much easier to read by the light of a 100-watt bulb than to squint using a 25-watt bulb.

Of interest in the conversion of liquid coatings, inks and adhesives to solids is the ultraviolet region of the spectrum, defined as 1.8×10^{-7} to 4.0×10^{-7} m (180 to 400 nm). A UV lamp's specific wavelength output is determined and controlled by the emission spectra of the given ultraviolet lamp. The lamp is often tailored to match the energy absorption of the reactive chemicals used in a given formulation.

Because ultraviolet energy is part of the electromagnetic spectrum, it can be referred to as radiant energy and the curing derived from it is referred to as radiation curing. Other portions of the electromagnetic spectrum also have industrial application. For example, gamma rays are used to sterilize medical disposable products. X-rays are used for diagnostic purposes. Infrared heaters are used to bake or cure coatings. In addition to being used for cooking, microwaves are used in the curing or crosslinking of some rubber products. Radio frequency heating is used to preheat moldable thermosetting materials. At specific assigned frequencies, radio frequency or dielectric heating is used to heat seal thermoplastic materials. These other areas of application give further support to the diverse and broad industrial acceptance of the industrial use of radiant energy.

In addition to being considered as a wave, radiant energy can also be characterized as particulate bundles of energy. From this viewpoint, the energy of any part of the electromagnetic spectrum is considered to be transferred by photons. The energy level of a photon is proportional to the frequency of the energy, namely:

$$E = h\nu$$

where E is the energy in ergs (10^{-7} Joules), ν is the frequency in cycles per second and h is Planck's constant = 6.63×10^{-27} erg-seconds. From the relationships given earlier, the following relationship can been obtained:

$$E = hc/\lambda$$

where c is the velocity of light, namely 3×10^{8} meters per second, and λ is the wavelength. From these equations, it can be seen that photons with higher frequencies (or shorter wavelengths) would have higher energy levels. Photons of the proper energy can interact with organic compounds called photoinitiators to produce energetically excited compounds which can subsequently induce or initiate curing reactions.

ENERGY TRANSFER BY SUBATOMIC PARTICLES

Atoms, the basic units of matter, consist of a core of outer shells of negatively charged particles called electrons and an inner nucleus which contains positively charged particles called protons and neutral particles called neutrons. In the stable state, the negative charges of the orbiting electrons are balanced by the positive charges of the protons. The configuration is analogous to the planets (electrons) orbiting about the sun (nucleus). Almost all of the materials found in nature exist in this stable state.

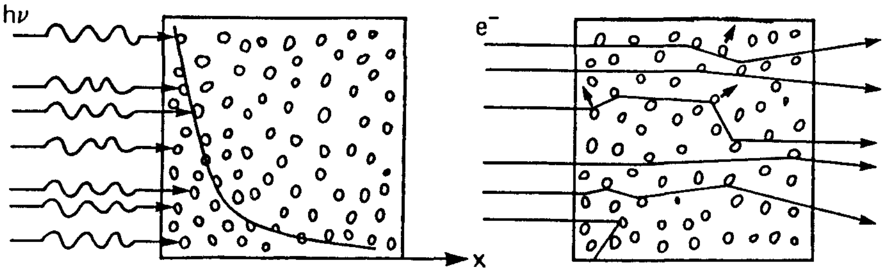
Some metals, like silver, copper and aluminum have the ability to give up electrons and then receive other electrons to permit the constant flow of electrons between two points. The result is the flow of electricity through a metal wire. While the flow of electrons is usually restrained to within a conducting material such as a wire, electrons themselves can be sufficiently accelerated to near the speed of light. This happens when a sufficient charge is built up by an excess of electrons in an object, such as a cloud, so that a sudden discharge occurs, as in lightning.

Using more controlled conditions, electrons can be made to flow from a source to a defined targeted material. This is the basic principle used in cathode ray tubes in which electrons are released by a filament and then directed to a surface, such as a television or a computer display screen. For these common applications voltage potentials are of the order of 40,000 volts and are sufficient to accelerate electrons within the CRT to impinge upon the phosphor coating on the screen and create a visual image

In the curing of coatings, inks and adhesives, electrons with slightly higher voltage potentials are used to initiate the curing. The voltage potential between the filament source of electrons and ground determines the kinetic energy or the relative acceleration of the electrons. Electrons in the range of 150,000 to 300,000 volts (150 to 300 KeV) acceleration have sufficient energy to cause the curing of the reactive materials in the ink, coating or adhesive.

Unlike the photon of ultraviolet light which tends to be absorbed mainly at the surface of the materials, electrons have the ability to penetrate through matter. Mass is the only thing that stops electrons traveling freely through space. Therefore, electrons can penetrate through foils and films used to laminate structures together as well as coatings and inks containing opaque materials. The extent to which electrons penetrate matter is determined by their voltage potential. The higher the voltage, the greater the penetration.

Ultraviolet Light and Electron Beam Penetration



Ultraviolet Light Electron Beam

Just as with radiant energy in the form of ultraviolet light, electrons also are useful in industry provided they are sufficiently intense. Wattage is also the unit of measure for the intensity of electrons. For all electron beam sources:

wattage = voltage x amperage

Since in commercial use the voltage is predetermined by the type of electron generator or accelerator and its setting, wattage becomes a direct function of the output amperage of the electron beam. Thus, the intensity of electron exposure can be controlled by the amperage, which in turn can be slaved to other processing controls such as line speed.

There are other industrial uses for accelerated electrons in addition to their use at 150 to 300 KeV to cure inks, coatings and adhesives. A large use for this technology is the crosslinking of the jacketing on wire and cable insulation. For this application, voltages of the order of 1,500,000 electron volts (1.5 MeV) are commonly used in order to assure complete electron penetration through the insulation wall. Shrink films, heat shrink tubings and the partial curing of tire components are other applications that use high voltage, high current electron beams. The use of 4,500,000 electron volts (4.5 MeV) for the sterilization of medical disposables is common practice.

ULTRAVIOLET LIGHT VERSUS ELECTRON BEAMS

Both ultraviolet light and electron beams are forms of radiant energy. Both are relatively easy to use and both can augment most converting operations. Ultraviolet light and electron beams are used in the curing or crosslinking of coatings, inks and adhesives. Being radiant energy, they can directly convert reactive liquids to solids and are not dependent on energy-intensive evaporation systems to remove solvent or water.

Besides the difference in penetration abilities already discussed, another difference between these two sources of energy is the relative cost of the equipment needed to generate the energy. There is approximately a threefold higher capital equipment cost for an electron beam accelerator compared to the capital cost for a full line ultraviolet system; however, the electron beam is often capable of operating at considerably higher line speeds, has greater penetration and cures opaque materials. Therefore, continuous long production run type of operations tend to favor electron beam technology, while operations that require material changes favor the ultraviolet curing technology.

Chapter Two

COMMERCIAL APPLICATIONS

INTRODUCTION

Ultraviolet and electron beam (UV/EB) curing, unlike other emerging technologies such as powder coatings for example, is limited by neither substrate nor application. UV/EB curable inks and coatings can and are being applied to essentially any substrate imaginable. Paper, wood, metal, leather, vinyl, plastic, glass, magnetic recording tape and even human teeth are substrates used in this technology. Application methods run the gamut from the more primitive "dip and wipe" to curtain coater, roll coater, silk screen, printing press and state of the art nitrogen-assisted airless spray.

The original driving forces behind the commercialization of the technology were energy savings and freedom from solvents. These benefits have been supplemented by the high productivity and subsequently higher profits that can be obtained with the industry's ever-increasing line speeds. Competition has provided the spark that has allowed the industry to overcome one technological hurdle after another. For example, in paper coatings, there are a number of coatings now available with good long-term shelf stability, cure stability, adhesion to a wide variety of inks, resistance to ink bleeding and low skin irritancy. It was not so many years ago that all of these properties were difficult to obtain. Table I shows the broad spectrum of markets which use radiation curable materials.

TABLE I: PRODUCT MARKETS FOR UV/EB CURING

COATINGS

Wood and particle board
Wood filler-particle board
Hardwood flooring

Wall paneling

Printed furniture laminates
Doors

Paper and board
Gloss coating for litho-printed paper
Record albums
Folding cartons
Conventional graphics
Magazines
Paperback books
Point-of-purchase advertising
Business forms
Bank notes and money bills
Release paper
Coated abrasive products

Rigid plastics
Letterpress ink for bottles
Vinyl flooring/tiles
Sheet vinyl floor covering
Screen printed bottles
Undercoat-vacuum metallizing
Plastic lens
Plastic cups — dry offset
Credit cards

Flexible plastics
Screen printed decals
Vinyl film, decorative paper laminates
Plastic tubes — barrier, decorative
Shrink film
Metallized film
Phonographic films
Magnetic recording media
Coated abrasive films
Release film

Metal
Can printing and coating
Lids and closures
Foil printing and coating
Nameplates
Screen printed metal signs
Magnet wire coating
Automotive spray coatings
Coil coatings

Leather
Topcoats
Finishes

Textiles
Sizes
Fill coats
Topcoats

INKS (Sheetfed, Web)

Lithographic
Magazine
Paperboard
Publication

Letterpress
Flexographic
Gravure

Screenprint
Poster/Display
Wall covering
Membrane switches
Backlit displays

PHOTOPOLYMER PRINTING PLATES

Letterpress
Flexographic
Gravure

ADHESIVES

Pressure sensitive adhesive and tape
Labels and decals
Laminating–wood grain panels
Automotive
Footwear, including flocking
Potting and encapsulation
Jewelry assembly
Glass product assembly

Transfer tapes
Laminating and packaging
Insulation
Abrasive bonding
Textiles
Nonwovens
Lamp assembly
Instrument and other product assembly

While the products in Table I account for the major portion of the radiation cure business, there are several high-value-added products that are used in low volume. They are given in Table II. The newest of these specialty products is the creation of prototype shapes using computer programs to drive an ultraviolet laser over a reservoir of coating to create a cured pattern. This cured area is then lowered below the coating surface with each pass of the laser to create complex three-dimensional shapes. This allows computer assisted design programs to directly create the part.

TABLE II: SPECIALTY PRODUCT MARKETS

Fiber Optics	*Medical/Dental*	*Prototype Modeling*
Glass	Casts	Complex shapes
Polymer	Fillings/caps	Forms
Couplings		Molds

These lists are not complete to be sure, as novel and ingenious new uses are being commercialized every year. The lists do provide an overview of some of the more common commercial applications and gives at least an idea of the scope and breadth of the technology.

ADHESIVES

Ultraviolet and electron beam curable adhesives represent a small but growing segment of the overall radiation curing market. They represent an increasingly attractive alternative to solvent-based, water-based and hot melt technologies. Structural adhesives, pressure sensitive adhesives, laminating adhesives and transfer metallization adhesives are all seeing increased usage. Many of the applications are quite sophisticated, such as electron beam cure transfer metallization adhesives for gift wrap paper. This process can be adjusted for either full sheet metallization or selective pattern graphic effects that simply cannot be duplicated by the more conventional processes such as metallic inks.

UV laminating adhesives have been slow to be commercialized in the United States as compared to Europe. Their ease of use, rapid cure, lack of solvents, and low energy requirements are beginning to interest laminators. The development of technology using cationic chemistry and visible light initiated systems is helping to overcome hurdles, such as laminating polyester film which absorbs most ultraviolet radiation.

Commercial adhesive products are produced on both UV and EB equipment. They include pressure sensitive tapes and labels, laminated foils and films, flocked materials for automotive and shoe applications, structural adhesives and abrasive bonding systems. The advantages of these adhesives are single-component materials that can be dispensed with automatic equipment, long “open time,” fast cures, lower energy requirements, ability to precision bond and low heat input to temperature-sensitive substrates.

ABRASIVES

Ultraviolet and electron beam curing is used in the manufacture of coated abrasive products for micro-finishing, glass lens grinding and polishing, burnishing and selected grinding products. Electron beam curing (EB) is also used in the manufacture of the filled fabrics used for cloth-backed coated abrasives. The existing thermoset resins are water-based phenol formaldehyde and urea formaldehyde resins. Their cure gives a highly crosslinked system similar to that produced using radiation curing. Unlike the rapid cure of the radiation based systems the thermoset cure can take up to eight hours in a carefully controlled oven with several temperature and humidity zones, followed by an additional post cure of 24 to 48 hours. The amount of energy required, and the time and amount of space required for the ovens, offer sound justification to convert to UV/EB curing wherever possible. At present, the formulated product costs and performance limit the applications to high value added abrasive products.

RELEASE COATINGS

The production of silicone coatings on paper and plastics is an example of the cooperation between oligomer producers, the curing equipment suppliers and the convertors. The major silicone resin producers worked with the equipment producers to identify radiation curable formulations that would match the existing release products. The convertors funded research in the application of the new products and invested in the equipment to produce the products. The result has been the conversion of several existing coating lines to UV/EB curing as well as the construction of several new lines.

METAL COATINGS

The use of UV inks and overprint coatings on two-piece metal cans has been commercially successful for several years. The production speeds obtained with UV cure are well above those with solvent or water-based systems. Two piece cans are printed by the dry offset process and flat sheet stock by lithography. White is usually the first ink down and interstation curing is used if the ink layer is heavy. Coating of three-piece composite and metal can ends has also been a commercial reality for several years. This application was one of the first large-scale uses of UV cure cationic epoxides.

A significant and rapidly growing application area involves the use of UV coatings with exterior weatherability for galvanized steel pipe for fence posts, highway guard rails, road signs, and parking meters. These coatings see severe service requirements in terms of their need to resist salt corrosivity, sunlight and moisture. Advances in UV absorbers, light stabilizers and a broader selection of aliphatic urethanes have enabled exterior weatherable UV coatings to become a commercial reality.

The use of exterior weatherable UV screen inks for such diverse applications as advertising signs, automotive decals and road signs is also seeing increased usage. Inks are formulated for the metal stock to be used, i.e., there are inks available for aluminum, tin plate, etc. For some applications an overprint coating may be applied in the final step.

Electron beam curing has been used to produce white coated stock for two-piece and flat sheet uses.

OVERPRINT COATINGS

Ultraviolet and electron beam curable coatings for paper substrates comprise approximately a $60 million dollar market in the United States alone as of 1994. Overprint coatings for plastic, foil and metal substrates add to this total to make the area of UV/EB overprint coatings one of the fastest growing areas. These coatings provide high gloss, high eye appeal (the wet look) finishes with both decorative and protective properties. Controlled gloss finishes such as flat mattes and satin finishes are also available. Selective pattern applied overprinting of a high gloss UV coating with a matte UV coating can result in some startling graphic effects that are seeing increased usage in many applications. In addition, the low temperature of cure prevents paper curl, and of volatile organic compounds are emitted.

These overprint coatings are now common in such end uses as book covers, greeting cards, magazines, cosmetic and liquor packages, corporate annual reports, calendars, record albums, folding cartons and catalogs. Application methods range from the state-of-the-art short delivery roll coaters and cylindrical screen presses to blanket coaters that can be retrofit onto existing presses. The application can be over wet or dry inks of the heat cure or UV/EB cure types. In applications such as tag and label work, in-line flexographic coating is becoming common. In sheet-fed offset type of work for applications such as folding cartons, greeting cards, and book covers, etc., wet trapping of the coating is also being done. Ultraviolet curable coatings are being used on the typical corrugated box to provide the wet look and increase visual appeal.

Current state-of-the-art involves total in-line operations. In UV curing, this means a high speed multi-color press whose last two stations are dedicated to an in-line IR dried waterborne size coat followed by a UV overcoat. In EB curing, the success of aseptic packaging operations has spawned in-line technology where several colors of EB inks are put down followed by an EB curable coating, all of which are then cured simultaneously by the electron beam.

Sheetfed lines using radiation curing run at speeds of up to 120 meters per minute (600 fpm), while web offset lines (such as magazine covers) may top 300 meters per minute (1500 fpm). The line speed is most often limited by mechanical and delivery limitations of the coating equipment rather than the cure speed of the coating. The need for the high speeds and specific service requirements (such as low odor for food-related packaging) have forced the development and commercialization of whole new classes of raw materials, such as polymerizable initiator systems and deodorized monomers and oligomers.

Equipment manufacturers have experience in retrofitting their equipment for UV and EB uses. While most installations for overprint coatings are UV, there are a number of commercial EB lines in operation. For porous substrates such as paper, EB offers the advantage of higher line speeds, thus reducing the "soak in" of the coating and allowing lower coating weights coupled with a low heat input. The low heat gain minimizes moisture loss by the paper stocks and maintains the flexibility. In conventional drying, moisture-sensitive substrates such as paper have required either controlled humidity drying or treatment to restore moisture after the heated ovens. Overprint coatings can also be used to seal porous surfaces prior to printing or coating operations. The coating should be formulated to accept the next layer to be applied.

FLOORING

After paper coatings, the flooring market accounts for the second largest usage of radiation curable coatings. A significant portion of this volume is captive manufacture by the flooring companies, but there is also a substantial commercial volume worldwide. UV coatings on vinyl flooring have been a commercial reality since the mid-1970s. In recent years, they have seen increased usage on wooden parquet flooring as well.

The premium no-wax vinyl flooring lines both in sheet and tile are coated with a clear UV topcoat. Generally, the topcoat consists of two layers, the first of which is a thin barrier coat to seal the vinyl and improve the adhesion of the second coating. The second coat or final surface layer is required to withstand abrasion and household stains, to be non-discoloring, and to be flexible and scuff resistant. The principle oligomer in this final coat is an aliphatic polyurethane acrylate or methacrylate. Each manufacturer has developed its own proprietary formulations to match its vinyl compounds. The coatings are formulated so that they can be applied after any embossing operation without the loss of the embossed pattern.

Wood flooring tiles are finished with a clear UV sealer followed by a UV topcoat. Again, the last coat usually contains an aliphatic polyurethane acrylate or methacrylate to provide the required abrasion or scuff resistance. After sanding, the assembled tile is coated with the UV sealer, cured and sanded again. After the surface is cleaned a UV coating is applied, cured and sanded. Depending on the grade and quality of the product, the process may be repeated. The UV topcoat is applied and cured, and the product is inspected and packaged for shipment.

WOOD FINISHING

The wood finishing industry was one of the first, if not the first, industries to embrace UV and EB systems on a commercial basis. UV fillers and topcoats for wood were used in Europe in the 1960s. The year 1971 saw the first commercial installation in the United States. The wood finishing industry has gained considerable experience in sealing, filling, edge filling and topcoating for particle board cabinets, panels and furniture. The use of radiation curing for finishing operations began with the low-end products based on particle board but has expanded to the top-of-the line furniture and wood products.

The three basic topcoats are based on polyesters, acrylics and urethane-acrylic blends. The polyesters were used in the beginning and continue to be used due to their lower cost. They are slightly less durable than the acrylic and urethane-acrylic systems.

Polyester topcoats applied at the thickness of 19 micron (0.75 mil) are cured at approximately 3 meters per minute (10 fpm) per 200 watts per inch lamp used. Using the same coating thickness and lamp power, the acrylic coatings are cured up to 6 meters per minute (20 fpm) and the urethane–acrylic blends cure at 4.5–6.0 meters per minute (15–20 fpm). The acrylic coatings are more expensive, but they offer better abrasion resistance and durability and are not as brittle as the polyester based coatings. The urethane-acrylic blends compete with the acrylics in cost and performance. They produce the most flexible of the three alternatives.

Today UV/EB curing for wood finishing applications can be divided into two categories: flat line finishing and three-dimensional curing of preassembled fine furniture.

Clear top coats, as well as pigmented gloss and low gloss mattes, are being used in flat finishing lines that utilize a combination UV/EB cure for gloss control. It is one of the very few large scale operations where a full hiding "paint" is being commercially cured by radiant energy.

Three dimensional curing of clear UV coatings is becoming more common with fine furniture. Concern over spray application and generally slower cure rates of the non-focused parabolic systems is being dealt with so as to make this application a commercial reality of increasing attractiveness, whereas it was considered of questionable feasibility not so many years ago.

FOOD AND PERFUME PACKAGING

This is a growing subcategory of overprint coatings, but it is of sufficient significance to warrant separate mention. UV overprint on folding cartons dates back to the 1960s, but the strong odor associated with many of the monomers, the amines, benzophenone and other initiators, made them unsuitable for many applications. Fine perfumes, chocolates, food packaging and restaurant menus were applications that were avoided because of possible odor problems.

The large scale commercialization of the aseptic packaging concept has led to the development of deodorized materials (both monomers and oligomers), polymerizable initiator systems and reactive amines which do not remain fugitive in the cured film, and therefore have substantially reduced odors. The comparatively recent development of these materials has expanded the marketability of the UV/EB technology into areas that were previously closed.

PRINTING

The advantages of a solventless resin system, such as stable color densities, and the ability to print fine line copy without drying in has made screen printing one of the fastest growing areas of this technology. UV overcoats are even being applied by the new generation cylindrical screen presses. These new presses advertise speeds in excess of 5,000 impressions per hour but are, in reality, limited by the UV coating's tendency to entrap air as it is forced through the screen at ever increasing speeds.

Finer reproduction (tighter registry), higher gloss and the ability to produce some unique graphic effects with pattern applied UV low gloss mattes screened over UV high gloss clear coatings has made this area very attractive to those looking for newer and bolder graphic effects.

Screen printing of UV inks is being done over paper, metal, films, foils, plastics and vinyl. UV/EB curable materials are being used as vehicles for ceramic inks that are screened onto automotive windshields, cured and then fired in an oven to volatilize off the vehicle and fuse the ceramic into the glass windshield.

Color rotogravure sections for newspapers, advertising supplements, catalogs, labels, inserts, carton stock, record jackets, book jackets and magazine covers are only some of the applications for narrow and wide web radiation curing. Application is by in-line systems, mostly UV with some EB curing, using single- to eight-station presses with either interstation or final cure. Substrates include paper, film and foil.

UV/EB curing has been used on most sheetfed presses. Conversion of older presses is difficult, due to the location of the lamp installation between the gripper bar chains and the stacker.

One of the most recent developments in printing uses a pulsed jet of ink that is electrostatically charged. This ink jet is directed by deflection plates in the printing head to produce a pattern. Both UV and EB curable inks are available for this printing method.

Flexographic printing using ultraviolet inks and coatings is routinely done on narrow web presses. The benefits of the technology have captured the interest of the wide web printers.

PHOTOPOLYMER PLATES

Research on photopolymers in the 1950s led to the introduction of photopolymer printing plates in the 1960s. The faster and easier processing of the printing plates and the improved printing quality of the plates resulted in a rapid acceptance by the printing industry. In the 1970s new instant printing shops based upon this technology began to appear in the marketplace. Production of photopolymer plates has been combined with computer technology to create desktop publishing. Photopolymer plates have led to improved quality in production of color separation and color reproduction.

Design of photopolymer plates is specific to both the type of press and type of ink being used. The suppliers to this industry usually supply additional graphic arts services and/or products to the printers. There are a number of products to choose from provided by over a dozen suppliers of materials and processing equipment. Plates are available for use with UV/EB curable inks and coatings. Plates are used with letterpress and flexography with perhaps the highest use on tag and label machines. Lithographic and gravure applications are determined by the length of the press run and quality of the reproduction required.

State-of-the-art photopolymer plates are generated directly by using a computer controlled laser beam to expose the plate. Thus no negative or paste up is required to provide the final press ready plate. This also allows printing to occur simultaneously at any number of sites.

The research developments in the photopolymer plate industry have benefited the development of UV/EB curable photoresists, adhesives and coatings.

ELECTRONICS

UV/EB curable materials see application in the electronics industry in the form of solder masks, photoresists, notation inks, encapsulants, conformal coatings to seal boards, potting compounds and various adhesives. Printed circuit board manufacturers can realize considerable cost savings from fast cure rates, reduced floor space, energy efficiency and lower capital cost.

Both positive and negative working radiation curing photoresists are commercial. The positive resists are used to create the fine geometries required for microelectronics. The continuing increase in complexity and need for miniaturization in chip manufacturing require high quality photoresists capable of images less than one micron. The requirements for negative resists used by the card and board manufacturers are somewhat less demanding. Boards generally require images of features in the 100–150 micron range (4–6 mils). Either system requires the formation of well defined lines.

Photoresists can also be divided into those which are subtractive and those which are additive in plating. The subtractive process uses the resist as a mask to protect the substrate from an etchant and the additive plating uses the resist as a form to define the plated area. Negative resists are applied by screen printing, roller coating or dry film lamination. For large volume operations the use of dry film resists has largely replaced screen printing. A dry film photoresist is usually a three-layer construction comprised of a polyester carrier film, the uncured photoresist, a release film (usually polyethylene) to prevent blocking. The polyethylene is removed prior to the hot roll lamination of the resist to the substrate. The polyester carrier film serves as a barrier between the hot roll and the resist. After exposure the polyester film is stripped prior to the "development" or removal of the uncured photoresist. The photoimage of the circuit can be produced by using a mask and low power UV source or by the use of scanned and pulsed UV lasers. The latter method uses the UV laser to draw the desired circuit on the resist.

In addition to the methods used for negative resists, positive resists are applied to silicone wafers by spin casting. This technique uses centrifugal force to produce a uniform coating.

Service requirements can be severe in that solder masks may be called upon to resist molten solder at temperatures approaching 300° C, to withstand chemical cleaning, to show no blistering, flaking or delamination in hot-cold cycling, and to be moisture resistant.

Some electronic uses are quite sophisticated such as the use of dry resist materials in micro-photolithography, where the resists allow selective ion implantation and etching, creating a multilayer sandwich of semiconductors on the silicone wafer. A single silicone wafer three inches in diameter may contain hundreds of microchips each of which contains hundreds of diodes.

DENTAL AND MEDICAL APPLICATIONS

Medical applications include such diverse applications as release coatings for transdermal drug delivery systems and surgical tape, and sustained release field wound dressings that incorporate micro-encapsulated antibiotics and coagulants in a UV curable urethane. This last application is relatively new and allows for the field application of wound dressings that protect the wound, deliver extended action or time release therapeutic agents and closely mimic the oxygen and moisture transmission characteristics of the human skin.

Another medical application is the partial curing of casts that can be shaped to the body part, prior to completing the cure by ultraviolet light. These casts are light and since they are shaped to the individual patient, they provide more uniform support than the corresponding conventional casts. They also provide less interference to X-rays than a metal cast and can be used with the electrical stimulation of bone knitting procedure.

Dental materials that are UV curable have been in use for some time and allow for longer working time and quick setting time, thus providing an attractive alternative to conventional materials. The majority of dental applications were originally restorative, but preventative applications are being commercialized. The dentist has time to match existing teeth colors and contours in his office without the use of casts and dental labs for many cosmetic applications. Special light sources with UV light guides are used to deliver long wavelength UV of approximately 360 nm. Exposure times range from 10 to 90 seconds depending on the thickness of the coating and the amount of filler used.

MAGNETIC MEDIA

The use of EB cured magnetic coatings allowed the development of the high density floppy disks and tape. Manufacture of these products is achieved by passing the uncured coating containing the magnetic particles through a magnetic field to orient the particles and then through the electron beam curing unit. The high loading of the magnetic particles prevents the use of ultraviolet cure for this application.

Electron beam curing offers several advantages to this market. The fast cure rate virtually eliminates the surface contamination problems associated with thermal curing processes. Because of the high pigment level, thermal cure systems have poor wear-resistance and durability. The highly crosslinked binders produced by EB give a tougher, more wear resistant surface. The problem of handling thin webs in a long oven is eliminated. The removal of the oven also reduces the possibility of the introduction of any heat memory or film distortion.

The production of magnetic media requires precision coating at its optimum level. The coating is applied in a clean room environment with precise control of both temperature and humidity. The techniques used to obtain the necessary tight control of the coating thickness and smooth surface required for data storage use are considered proprietary to the manufacturers.

With all the advantages of EB curing to this market, why have the predictions that EB curing would dominate this market failed to materialize? Erosion of pricing of conventional magnetic media coatings coupled with technical concerns about adhesion have generally created a reduction in interest. At present, EB curing only accounts for a small segment of the market.

FIBER OPTICS

The use of optical fibers as data transmission media replacing coaxial cable systems has resulted in a very healthy growth rate of one of the more technologically challenging applications of ultraviolet curable coatings. Beyond the normal requirements of adhesion and flexibility, optical fiber coatings must be formulated to protect the delicate fiber for over 30 years. Since the fiber serves as an optical wave guide, the coating has to impart enough resistance to lateral deformation to prevent signal attenuation. Physical toughness, scratch resistance and freedom from tack are also necessary properties. The durability of the coating is also important since the coating will protect the fiber, whether it be glass or plastic, from damage which could occur in handling and installation.

The use of two coatings allows optimum performance. The first coating is a thin coating which acts as a buffer for the fiber. The second, outer coating provides the mechanical properties necessary to protect the fiber. Ultraviolet curable inks are used to color code fibers, and UV adhesives bond fibers into ribbon-like structures

UV curing has allowed increased production rates, and as with other application areas, this increased productivity translates to lower costs.

PROTOTYPE MOLDING (STEREOLITHOGRAPHY)

Production of three-dimensional models using UV laser curing of radiation curable materials became commercial in the late 1980s. The model is built up using successive scans of a computer-controlled laser beam on a pool of coating. The cured coating is deposited initially on a platform. As the model is built up by the cured resin, the platform is lowered into the resin pool so that fresh uncured coating covers the surface of the model. This is, in concept, an advanced three-dimensional version of the photopolymer plate process. Once the model cure is complete, the uncured coating is washed from the model and a second ultraviolet cure may be applied. The model can be completed using the standard shop procedures.

MISCELLANEOUS UV/EB CURABLE PRODUCTS

Commercial products based upon this technology in addition to those listed above include:

- Textiles: sizing, filling, and topcoats
- Leather: topcoats and fillers
- Topcoats: for hubcaps, galvanized metal tubing, glass bottles, solar energy cells, glazing panels, etc.
- Caul sheets: plastic molding
- Optical disks
- Ceramic binders
- Fiber reinforced plastics: glass binders, FRP sealer, and topcoats
- Wire and cable: enamels, coatings, cable fillers, moisture barriers
- Encapsulation
- Conductive cements
- Semipermeable membranes

SUMMARY

The many benefits which have caused the commercialization of the variety of products described above is counteracted by higher material costs, line of sight curing, depth of curing, cost of EB equipment, potential skin irritation, not as yet FDA status and crosslinking limiting rework.

There are many applications for which radiation curing can be commercially used to benefit the convertor and to improve product performance. These benefits can only be realized when all parties to the process, i.e., the raw material suppliers, the formulators, the application and curing equipment suppliers, the fabricators and convertors, and the customer, are educated in the principles of radiation curing technology.

Chapter Three

ULTRAVIOLET AND ELECTRON BEAM CURING EQUIPMENT

RADIANT ENERGY FROM ELECTRICITY

Electron beams and ultraviolet light are generated from electrical sources. As part of the electromagnetic spectrum, they are forms of radiant energy. Unfortunately, the ill-informed, by word association, confuse radiant energy or radiation cure with radioactivity or nuclear radiation.

While nature showers the earth with diffuse radiant energy in the form of sunlight, it also permits some aberrant materials which in their own right emit radiation. Radioactive materials like uranium and radon gas are found in the environment, but fortunately in relatively minute amounts. These sources of radiation require extreme caution in handling and are not involved with UV/EB curing.

From the study of such naturally occurring sources of energy and an understanding of the functions and use of electricity, physicists and engineers have developed electrical devices which can convert ordinary electrical power, such as that commonly available in factories, into radiant energy. For companies processing coatings, inks and adhesives, no special power source nor safety construction is needed to take advantage of either ultraviolet light or electron beam energy. The commercially available sources for these two types of energy fit right into the workplace and pose no special operational concerns.

Based upon such conversion of line current or ordinary factory electrical power to either ultraviolet light or low energy electron beams, these energy sources can be designed to avail themselves of the latest in electromechanical interlocks. A power interruption as simple as throwing a switch or pulling a plug can safely shut down either type of equipment. Being electrically powered, energy sources can also be designed to automatically shut down in the event of some malfunction with a coating or printing unit. Sensors for web breaks or for detecting low levels of ink or coating material can also be used to shut down these electrically powered units.

In contrast to convection ovens which have been used to drive off solvents or water and to apply heat to cure coatings, inks and adhesives, ultraviolet and electron beam energy interacts directly with specially formulated materials which are often applied as 100 percent liquid systems, containing low levels of volatiles. This direct action initiates a chemical reaction in fractions of a second. The space required for either an ultraviolet or an electron beam curing unit is considerably smaller than that required for convection ovens, especially when used in wide web, high speed coatings and laminating operations. With UV/EB curing, electrical energy is efficiently used and no costly solvent recovery or emission control systems are needed.

ULTRAVIOLET LIGHT SOURCES

Fluorescent lighting is our most common experience with the technology used to generate ultraviolet light of the kind needed in the processing of coatings, inks and adhesives. A fluorescent light bulb consists of a long tube filled with an ionizable gas, a gas which can be excited by electricity. The glow from said gas is absorbed by a coating on the interior surface of the bulb which in turn fluoresces or emits light. By careful choice of this interior coating, light output in the visible range of the spectrum can be maximized, while an excess of ultraviolet light is reduced. Adequate lighting can be attained from as few as 40 watts over a one-meter-long bulb.

To effect the conversion of specially formulated coatings, inks and adhesives by ultraviolet light, a far more intense light source is required. Output intensities as high as 120 watts/centimeter (600 watts/inch) are available. [This would be equivalent to 12,000 watts per meter!] To achieve this, all reputable suppliers of ultraviolet light radiant energy equipment rely on some basic components:

a) the light source, typically a tubular glass bulb.
b) a power supply, needed to energize the bulb.
c) reflector systems used to focus or diffuse the light.
d) a way to prevent light from hitting a target, such as a shutter system.
e) cooling techniques to remove heat from the lamp area.
f) safety shielding to prevent stray light from being emitted into the workplace.
g) a conveyance system for transporting a product.

The nature of the process and the shape of the substrate dictate the type of ultraviolet lamp system to be used, the type of reflectors and power supply needed and how the ultraviolet lamp is energized, either directly by electrodes or in a controlled microwave field.

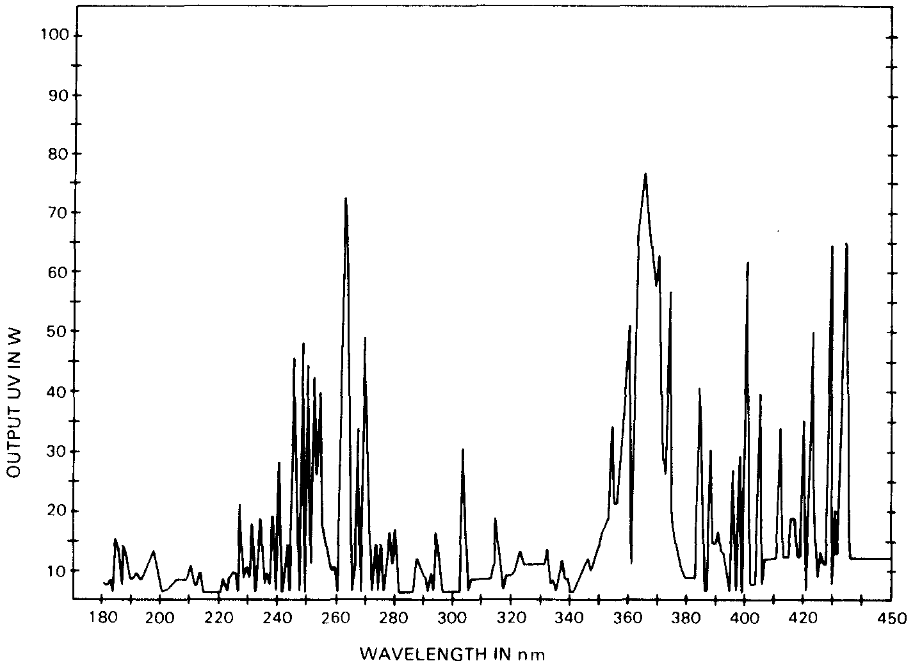
All well-designed ultraviolet light energy sources are housed in units which prevent extraneous light from reaching the workplace and posing possible problems of eye exposure to the ultraviolet light. Suppliers who are more concerned over saving costs may not give sufficient attention to housing their units in light tight enclosures and may downplay this important design feature.

Suppliers of ultraviolet light radiation curing equipment to the myriad of applications often differ by offering unique approaches to some of these systems components. These differences are often found in the electrical supply to the bulb, the cooling of the bulb area and unit, shielding of the substrate from unwanted energy and the interface of the bulb control system with other process controls. A given supplier of ultraviolet equipment may have optimized his unit design for a particular end-use market segment. These factors should be taken into account when selecting a vendor and equipment.

THE ULTRAVIOLET LAMP BULB — THE SOURCE OF LIGHT

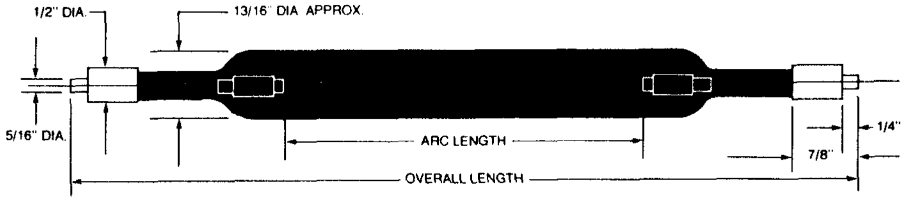
When an inert gas mixture, often consisting of argon, neon and some mercury vapor, is contained in a sealed quartz tube and subjected to an electrical field, it can become charged, or ionized. As the voltage potential across this field increases, the temperature of the gas also increases. As the temperature increases, the small amount of mercury present in this mixture vaporizes and enables the mercury to also ionize. Thus, a mercury vapor arc is created within the sealed unit. One of the unique properties of this arc is its high emission of light in the ultraviolet regions of the spectrum. In particular, intense emissions are noted between 240 and 270 nm and between 350 and 380 nm. It is this intense light beyond the violet region of the visible spectrum (thus ultraviolet) which has sufficient energy to interact directly with specific photo-active chemicals (as will be described in the chapter on chemistry). At full operating power, some visible light as well as some infrared energy is also emitted.

Spectral Output from a Mercury Vapor Lamp



Sealed tubes of fused quartz are used to contain the start-up gas and the mercury vapor. These tubes or bulbs have a wall thickness of about 1 mm with outer diameters ranging from 8 to 10 mm up to 20 to 25 mm. Lengths of up to nearly two meters can be obtained for the typical medium pressure mercury vapor lamps. Fused quartz is used for these bulbs because of its optical purity in the ultraviolet region. This permits maximum output of the desired wavelengths of light. Ordinary glass, such as that used for windows and ordinary light bulbs, absorbs ultraviolet light.

Typical Mercury Vapor Ultraviolet Bulb



In order to sustain a balance between having a sufficiently intense light source of 100 to 120 watts/cm and at the same time keeping the spectral emission primarily in the ultraviolet range, the fused quartz bulbs are pressurized to about two atmospheres (1,520 mm of mercury). Lower pressures can be achieved by using less mercury, but this in turn diminishes the available mercury vapor and reduces the watt density of the bulb. At internal bulb pressures above two atmospheres, there is a spectral shift toward the less desirable red and longer wavelengths.

While the mercury vapor arc is itself several thousand degrees centigrade, it is important to maintain the bulb surface temperature within certain bounds. The target bounds are usually between 600° C and 800° C. The lower limit is desirable in order to maintain internal bulb pressure and thus watt output density and to assure the complete vaporization of the mercury. Therefore, bulb cooling systems must be carefully designed so as to prevent excessive surface cooling which in turn would cause some of the mercury within the bulb to condense and thus reduce the bulb's efficiency. While quartz itself melts at 1,700° C, the process of devitrification or change in quartz crystal structure, which begins near 1,000° C, must be avoided. Such changes in the crystal structure of the quartz cause gray areas to appear and greatly diminish the optical transparency of the walls of the bulb.

The control of bulb surface temperature as well as the internal bulb pressure and mercury arc intensity are all taken into account in the design of a system for providing ultraviolet light energy. A user, however, must be constantly aware that an operating ultraviolet source is hot. Should a malfunction occur, the bulb itself must be allowed to cool or be handled only with insulating gloves. Care must also be taken to see that the bulb and reflector surfaces remain clean. Oils from fingerprints or even the accumulation of other trace organic matter can accelerate the deterioration of the quartz.

Some manufacturers of ultraviolet lamps have further modified the composition of inert gas and mercury used to generate light by putting additives or dopants into the bulb. The function of these proprietary dopants is to shift the spectral output of the bulb into other wavebands generally within the ultraviolet region. Some dopants are used to reduce the infrared emissions which are normally given off by a mercury arc and will generate heat in a substrate. Other dopants are used to adjust the spectral output of a lamp so as to optimize the efficiency of its output in activating a specific photo-active chemical. This results in increased energy efficiency and permits the highest web speeds per watt density. Lettered designations, like D, X, M, V and A, are used to identify these specially doped bulbs. Discussions with the vendors of these bulbs should be held to determine their suitability in a given process.

THE POWER SUPPLY

Most medium pressure mercury lamps used to generate ultraviolet light have electrodes at each end of the quartz bulb. These electrodes and their contacts are smaller in diameter than the diameter of the bulb. In fitting into their sockets, these contacts also position the bulb appropriately within the reflector. The techniques for making these electrodes and contacts are proprietary to each bulb manufacturer. Because the bulb operates with an internal pressure and at elevated temperatures, great care is taken to assure that an excellent seal is maintained between the quartz housing and the metal of the contact. Maintaining this seal during the thermal cycling encountered during bulb start-ups and shut-downs has a great influence on the longevity of the bulb. Care is taken to see that these contact ends of the electrode lamps are not exposed to excessive temperatures during operation.

Power is supplied to the electrode lamp through a ballast which consists of a transformer and capacitors. This type of system is designed to compensate for fluctuations in line voltage so that the power to the lamp during operation remains constant. Most ballasts supplied with ultraviolet systems operate in two or three modes:

1) A high voltage is needed in order to warm the gas and vaporize the mercury and generate the arc in the bulb. During this warm-up period, which can take from two to three minutes, a current-limiting device must also be in the circuit to prevent excessive current flow.

2) A lower voltage with constant current is needed in order to sustain uniform light output during operation.

3) A cut-back or half-power condition is useful so that the bulb can remain glowing, but not at peak output, during down time. Excessive start-ups and shut-downs of medium pressure mercury electrode lamps can greatly reduce their service life.

In general, one ballast is required for each lamp being used. However, in some instances, two lamps may be run off of a common ballast. These power supplies are quite efficient. Approximately 90 percent of the line input power is delivered to the lamp in an electrode connected system.

An alternative to lamps using a ballast and an electrode is the electrodeless system. This unique system activates the gas within the quartz bulb in a microwave field created by small magnetrons, similar to that found in a common microwave oven. As a result, there is no direct electrical connection between the bulb and its housing. In this way, the ends of the bulb can be self-fused quartz, thereby eliminating the sensitive quartz-metal seal of the more common electrode bulb. Short stubs are at each end of the electrodeless bulb in order to provide mechanical support for mounting the bulb in the unit. Most electrodeless bulbs used in printing and converting operations are limited to 24 cm (9.6 inches) in length. For wider web processing, a series of these electrodeless lamps are installed in a row.

In relying on microwaves to activate the gases in the bulb, full power can be attained within 10 seconds, in contrast to the several minutes needed to start up the electrode bulb. In addition, repeated or multiple lamp start-ups appear to have little effect on the anticipated life of the electrodeless bulb. As a result, there is no need for a stand-by or partial shut down condition. Furthermore, bulb warranties for the electrodeless bulbs tend to run nearly three times longer than for the conventional bulbs, 3,000 versus 1,000 hours at >85 percent rated output.

The units which provide the microwaves to activate the electrodeless bulbs are self contained and fully shielded to prevent stray microwave emissions from entering the workplace. These units are available in modules capable of holding a standard 24 cm (9.6 inch) long bulb. Wider sheet or web applications are accommodated by ganging a series of these units in a row. There is sufficient dispersion of the ultraviolet light at the ends of these units to render a uniform level of exposure across a substrate.

In summary, the conventional and electrodeless ultraviolet lamp systems offer:

	Conventional Electrode Lamp	Electrodeless Ultraviolet Lamp
Watt density:	120 watts/cm	120 watts/cm
Bulb length:	up to 2 meters	24 cm
Power source:	transformer and capacitor ballast	proprietary microwave system
Start-up time:	2 to 3 minutes	10 seconds
Stand-by condition:	half power	none required
Lamp warranty: (>85% output)	1,000 hours	3,000 hours

THE REFLECTOR SYSTEM

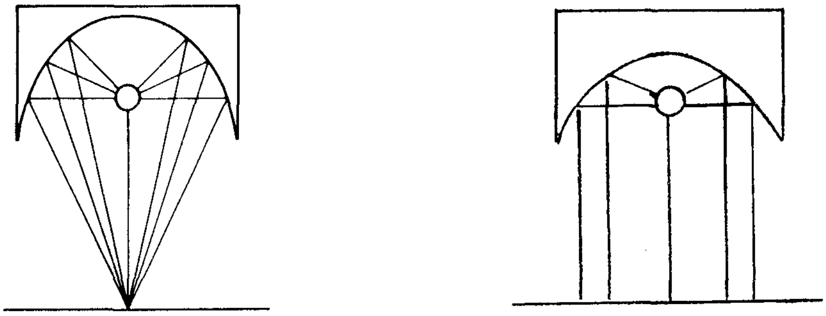
Depending on the end-use application, it is sometimes desirable to concentrate the ultraviolet radiant energy on the target substrate, such as in running high throughput converting operations. In some other applications, such as in the deposition of ultraviolet light on three-dimensional objects, it is desirable to diffuse the light to attain a more uniform crosslinked or cure state in a coating.

The common practice for concentrating ultraviolet light onto a target substrate is to position the bulb at one focal point within an ellipsoid. An end segment of the ellipsoid, fashioned out of stainless steel or highly polished aluminum, is then made to serve as a reflector. With the bulb centered at one focal point, the laws of optics dictate that the highest intensity of reflected light will be at the other focal point of the ellipsoid. Thus, one can focus the maximum intensity of ultraviolet output at a point or line approximately 1 cm wide, traversing a web or sheet perpendicular to the bulb.

The geometry and dimensions of the ellipsoidal reflector will dictate the distance one must maintain between the bulb and the target substrate in order to sustain this focus. Any raising or lowering of the target substrate will diffuse this focus and diminish the intensity of the ultraviolet light received by the substrate. Intense light is desirable in high speed, high throughput operations. The distance from the lamp to this second ellipsoidal focal point or to the substrate will be specified by the lamp vendor.

Since all commercial ultraviolet sources also emit some visible and near infrared or heat energy, such light energy will also be concentrated at the second focal point distant from an ellipsoidal reflector. In order to reduce this heat input, especially if dealing with heat sensitive substrates, one may opt to use a parabolic reflector in which the bulb is at the focal point of the parabola, which can be designed so that the light will be reflected outward in nearly parallel rays. The width of the band of the emitted ultraviolet light will then depend on the dimensions of the parabolic reflector itself.

Ultraviolet Light Reflectors



Elliptical Parabolic

In situations in which diffuse ultraviolet light is desired, as in the converting of coatings on three-dimensional objects, the use of parabolic reflectors would be preferred over attempting to diffuse the light by adjusting the distance between the source and the substrate. Diffuse light is desirable when dealing with shaped or three-dimensional objects because such objects have surface irregularities which can be more uniformly exposed when subjected to diffuse rather than concentrated light.

DEALING WITH HEAT OUTPUT

As noted, even with the most tailored and doped mercury vapor ultraviolet light sources, there is an emission of some infrared or heat energy. Not only because of the need to maintain controlled temperature conditions in and around the bulb, but also because of substrate considerations, the temperature of an ultraviolet source must be tightly controlled.

During operation, ultraviolet sources are most commonly kept cool by the circulation of air through plenums on the back of the reflector. With electrode attached bulbs, such cooling air is also circulated toward the bulb sockets so that excessive heat does not build up in these sensitive areas. Even with the electrodeless design, the heat absorbed by the metal of the reflector must be removed. An alternative to the use of cooling air is the use of a combination of circulating air and water. With some reflector designs, the plenums on the backside of the reflector are made to carry cooling water, which is a more efficient heat transfer medium. The newest method of heat removal is the use of special dichroic reflectors.

At first glance, one might think that a filter could be used to eliminate the unwanted infrared or heat energy. However, any optical filter capable of removing these higher wavelengths would also diminish the intensity of the ultraviolet light energy. One proprietary system interposes quartz tubes filled with circulating deionized water between the ultraviolet light source and the substrate. The water supposedly absorbs nearly 95 percent of the infrared energy and is recirculated through a heat exchanger. This prevents unwanted heat from reaching a substrate.

Often the speed of a web or sheet traversing under an ultraviolet source is sufficient to prevent any heat build up within a substrate. Obviously, black bodies and soft substrates, like plasticized vinyls, will require some care. Such materials can be handled atop a cooling drum, chilled by circulating water, which is positioned directly under the light source. For sheet-fed materials, the conveyor used is often a metal linked belt. This design prevents the conveyor itself from becoming heated. When an inert gas atmosphere is used to enhance the rate of reaction of a photo-reactive material, the gas itself can serve as a substrate coolant.

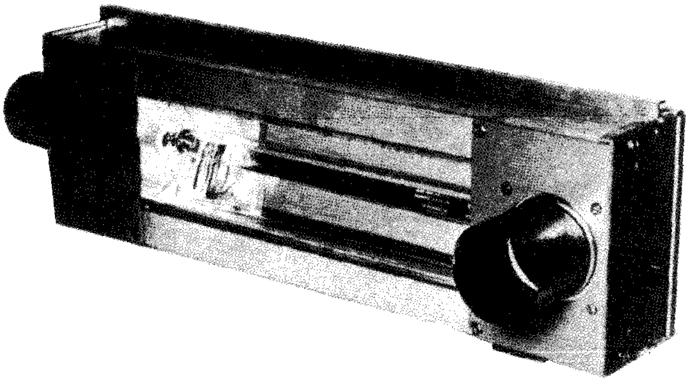
Some practitioners of ultraviolet curing have learned to take advantage of the heat output from the ultraviolet source. Since the rates of chemical reactions increase with temperature, the heat energy from the ultraviolet lamps is used to enhance the reaction rate of the photo-reactive chemistry. This thermal bump can be used to increase line speeds or running rates. However, discussions should be held with the vendor of a particular coating, ink or adhesive to verify that an added heat input would indeed work with the ingredients in a given formulation.

When an electrode type ultraviolet source is down for short periods of time, such as during a web-splice or change or during the intervals between successive sheet exposure, most units can be turned down to a lower current draw and maintained in a stand-by mode. This eliminates the complete cycling of the unit between on and off and reduces the thermal and electrical stresses on the components.

Highly focused, high intensity sources may emit enough thermal energy to cause damage to a stationary or non-moving substrate or even to ignite a combustible material like paper. Thus, a mechanical shutter system is sometimes provided with lamp systems as an added safety feature. A shutter can be interlocked with a web sensing device so that in the event of a web break, the shutter can be immediately activated and prevent the heat output from the source from striking a substrate or target material. The combined use of a shutter system and the current drop of a stand-by mode is good for short term production interruptions. For long down times of several hours, it would be better to shut down the ultraviolet source entirely.

The combined assembly of an ultraviolet source, its power supply, its reflectors and cooling system is often referred to as an ultraviolet irradiator. Such assembled units are manufactured by a number of reputable suppliers who take care to see that no extraneous ultraviolet light is emitted into the workplace.

Air-Cooled Ultraviolet Irradiator



ULTRAVIOLET CURING SYSTEMS

When compared to air convection ovens used for solvent or water removal, ultraviolet light energy sources are relatively compact. Depending upon the end-use application, an ultraviolet unit can be either a stand alone device or an addition to an existing process unit or it can be incorporated directly into the design of a piece of converting equipment, such as an office copier.

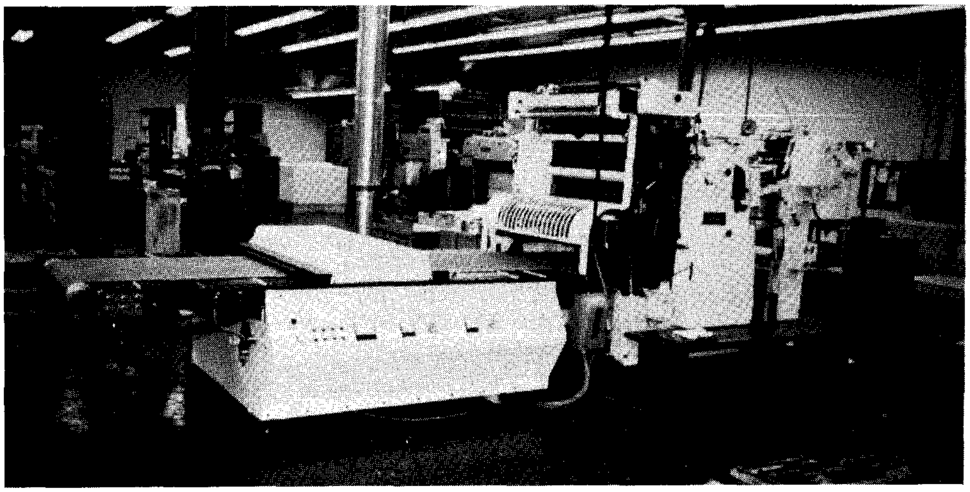
Stand-alone ultraviolet devices are useful for research and development purposes. Here, narrow conveyor belts can be used to transport small samples under an ultraviolet source. Such development equipment is useful not just to the suppliers of ultraviolet reactive materials, the vendors of coatings, inks and adhesives and their raw material suppliers, but also to major end users. Knowing the energy output of the light source, the conveyor speed can be varied so as to determine an optimum set of operating conditions for a given combination of substrate, photoreactive material and lamp intensity. Such rate data, usually expressed in meters or feet per minute, can be used in determining the intensity and number of ultraviolet units needed for a given production operation.

Stand-alone units are also used with sheet-fed materials. Photoresists on metals, screen printed posters and even some three-dimensional objects can all be exposed to ultraviolet light on large sized units which come complete with their own conveyor system. Units nearly as wide as two meters are possible. For increased production rates, multiple rows of ultraviolet units can be positioned parallel to each other. Two or three rows of ultraviolet sources would double or triple the output for sheet-fed materials.

With three-dimensional objects, sophisticated conveyance systems can be designed so that combinations of different banks of ultraviolet sources can be used in conjunction with the rotation of the object to be exposed. This will permit the complete curing of a coating or ink on complex shapes at effective production rates. In dealing with three-dimensional objects, care must be taken to position the object in front of the source or sources so that the object itself does not impede or shadow the ultraviolet light from hitting the entire surface. Attention must be given to the angles of presentation and to the rotation of the object. As noted, diffuse ultraviolet light might be more effective in these applications.

In web printing and converting applications, ultraviolet sources can be positioned immediately after a printing station or coating head. Such units take up very little line space. In wide web converting situations, conventional electrode ultraviolet sources are available with bulb lengths up to nearly two meters. One bulb would be sufficient to cover a nearly two meter wide web. When used with multi-color web printing, ultraviolet units can be easily mounted onto a given printing station to set or cure a color immediately after it has been printed and before another color is applied. Likewise, banks of lamps can be mounted at the end of a press to cure overprint varnishes and/or to set the ink system more completely. The capital costs for an ultraviolet radiant energy source are relatively small when compared to the total costs of a converting line or printing press.

Ultraviolet Light Curing of an Overprint Varnish



It has been estimated in the United States, nearly 500 companies were using ultraviolet light curing near the end of the 1980s. Ultraviolet light curing was being mainly used to cure thin coatings and inks (about two-thirds curing <25 microns or <1 mil thicknesses). In production operations, about half the ultraviolet light curing lines were running at 30 meters (100 feet) per minute or less, however, some lines were achieving line speeds in excess of 180 meters (600 feet) per minute. Although most ultraviolet curing lines are <60 centimeters (24 inches) in width, a few are as wide as 180 centimeters (72 inches), which indicates the wide web capabilities of this curing technology.

ULTRAVIOLET LIGHT SOURCE VARIATIONS

Most of the major industrial end uses of ultraviolet radiant energy for the curing of coatings, inks and adhesives are covered by the sources described above, however, there are some variations worth noting:

POINT SOURCES

Hand held point sources of ultraviolet light are available for use with adhesive systems which can be photo-activated. These sources draw only about 75 watts of power and emit around 50 to 70 milliwatts/cm^2 of ultraviolet light at 365 nm. A fiber-optic lens assembly is used to guide the light to the target. These point sources are used in splicing fiber optics, in fastening critical items like lenses, in bonding materials to printed circuit boards and in encapsulating small electronic components.

PULSED XENON LIGHT

One is familiar with the use of strobe lights to determine the running rates of high-speed moving equipment or to jazz up the visual effects at discotheques. When used with an ultraviolet source, such as a bulb filled with xenon gas or xenon and a dopant, a pulsed light system is capable of delivering much higher intensities of light over a comparable time frame than the standard continuous radiation sources. For example, with a continuous source, 500 watt-seconds of energy (500 Joules) is delivered by a 500 watt source in a second. With a pulsed system, 500 watt-seconds of energy can be delivered in a millisecond or one one-thousandth of a second. By controlling the pulse rate, one can significantly increase the amount of energy delivered to a target over a given time frame. One can also use the pulse rate to fine tune the energy output to the photo-response of different chemical materials.

Because of its inherently higher costs, pulsed light is used primarily in specialty applications. Hand held or small target sources are used to expose areas of less than 2.5 cm by 2.5 cm (one square inch). This approach has found use in the optical and electronic markets. Specialty wide web and coating applications have also benefited from the use of pulsed ultraviolet light. The pulsing of the light itself tends to diminish the heat input to a substrate and there is some evidence that these higher energy levels of light have greater penetration through transparent films and coatings than continuous ultraviolet light.

SHAPED BULBS

While the most common ultraviolet lamps use straight tubes of quartz, it is possible to shape the quartz tubes so as to distribute the light over greater cross-sectional areas or even around three-dimensional objects. When using this approach, a great deal of attention must be given to the thermal output of a system. It is much easier to design reflector and air cooling systems around linear bulbs. Shaped bulbs, however, must still be maintained within the temperature bounds discussed above. In this regard, the use of pulsed light with its inherent cooling pauses may be more effective with shaped lamp systems.

Ultraviolet sources can also be fashioned into high intensity point sources or spherical bulbs and positioned within conical reflectors for delivering light to small areas. Such spherical bulbs are even available with the electrodeless technology. Graphic arts applications which demand a high degree of resolution have used these sources.

GERMICIDAL LAMPS

Low cost, low intensity germicidal lamps have found some use in laboratories wherein they can be effectively used for screening and quality control purposes. The watt intensity for germicidal lamps is considerably lower than that of commercial production units, ranging between 0.4 and 4.0 watts/cm (1 to 10 watts/inch). Thus, care must be exercised in extrapolating any data from germicidal lamp exposure.

ELECTRON BEAM ACCELERATORS

In a cathode ray tube, such as the picture tube of a television set or the display screen of a computer, a direct current potential is established between a filament or cathode which contains a high excess of electrons and a positive terminal with a slit or hole in it which is connected to ground. As the voltage between these two poles increases, say to 40,000 volts, electrons are drawn away from the cathode toward the ground. Because of their high voltage potential, these electrons travel at relatively high velocities. The open design of the anode or ground allows most electrons to pass right through an anode ring and travel freely until stopped by matter which, in these examples, is the phosphor coating on the interior of the front of a screen. Pictures or characters are generated by controlling the horizontal and the vertical sweep or scan of this electron stream.

The photons emitted by ultraviolet light sources travel at the velocity of light irrespective of wavelength. These photons, however, have only relativistic or minuscule mass and are easily stopped at the surfaces of materials. Electrons, however, have more measurable mass, but do not of themselves travel at the speed of light. As the voltage potential between an electron source, a cathode or filament, and ground increases, so too does the velocity and kinetic energy of the electrons in free space.

By increasing the voltage potential to 100,000 volts or even up to several million volts, electron velocities begin to approach the speed of light. It is at these higher voltages, say between 150,000 and 4,500,000 volts (150 KeV and 4.5 MeV), that practical industrial applications have been found for these accelerated electrons. At these voltages, electron beam accelerators have been built which are capable of delivering high beam currents or sufficient amounts of electrons over a given time frame to be of economic consequence.

For the most part, the higher voltage electron beam accelerators, say >300,000 volts, rely on a scale-up, considerable as it may be, of the basic cathode ray tube principles. A point source of electrons or beam column is magnetically scanned in one direction in order to spread out the electron beam so that it can interact with a greater cross-section of material. Scan widths of up to 1.5 meters have been attained. The equipment designed for such higher voltage accelerators differs among suppliers in the kinds of transformer systems used. These higher voltage systems are quite large and are almost always set up as stand alone operations and require large concrete shielding facilities.

While some 150,000 (150 KeV) to 300,000 (300 KeV) volt electron beam accelerators based on these scanned beam principles have been used to convert coatings, the majority of installations in this voltage range rely on linear cathode concepts. These accelerators have a number of common features:

a) transformers and a DC power supply.
b) linear filaments differing in design configuration between vendors.
c) an evacuated acceleration tube or chamber with a separate vacuum system to maintain said vacuum.
d) a beam window.
e) lead safety shielding around the acceleration tube and under beam transport systems.
f) electrical control systems for interlocking beam operations with other process equipment.

THE POWER SUPPLY

Coil wound transformers are used to provide the voltages needed by linear cathode electron beam accelerators. These transformers rely on standard factory current. Depending upon the power level of the accelerator, relatively small transformers can be used as in small scale, self-contained lab units. Larger transformers, sometimes occupying as much as one square meter of plant floor space, are needed for high current production units. These transformers may be either oil filled for insulation and cooling or can rely on sulfur hexafluoride gas as a coolant/insulator. With production units, the transformer is connected to the accelerator by a high voltage cable. Thus, the transformer can be physically located well away from the accelerator.

FILAMENT SYSTEMS

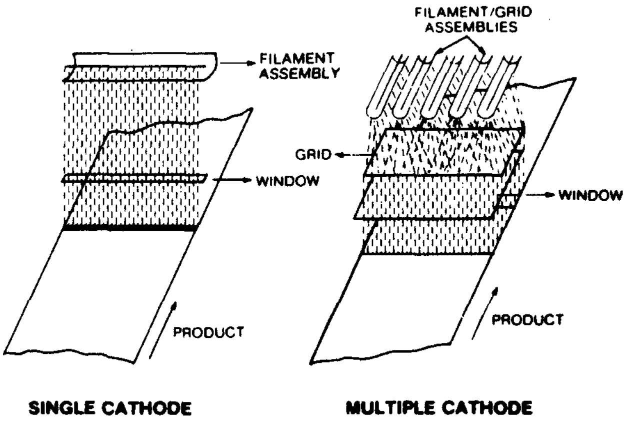
The key to compact electron beam accelerator design in the low voltage, 150 KeV to 300 KeV, range is the use of linear filaments which eliminate the need to scan electrons. Two basically different approaches have been taken to designing filaments out of flat structures which traverse across a web.

In one approach, a continuous filament is formed and cut to length so that the filament itself approximates the width of the application area. With this design, the filament is able to emit a shower or curtain of electrons uniformly across a given area. Extending the target width of an accelerator becomes a matter of building longer filaments and the support structures needed to hold them and the accelerator housing. This curtain approach permits building accelerators capable of depositing electrons on webs up to two meters in width.

For some applications which require both a high production throughput and a high level of beam exposure (a moderately high dose), parallel filaments can be aligned within the same acceleration chamber. Acceleration heads with up to four such parallel filaments have been built to crosslink the binders used in making magnetic tapes.

The other approach to filament design is to run many short filament lengths in the direction of the web which are in turn connected to each other in parallel. In this configuration, the filaments tend to broaden the beam of electrons impinging upon a target substrate. Since these filaments are assembled in modules, a number of modules can be linked together to permit the electron bombardment of webs well in excess of two meters in width, approaching nearly three meters. Given the other design features of the acceleration system and its necessary lead shielding, structural considerations tend to limit the practical web widths which can be treated with electrons.

Electron Beam Filament Constructions



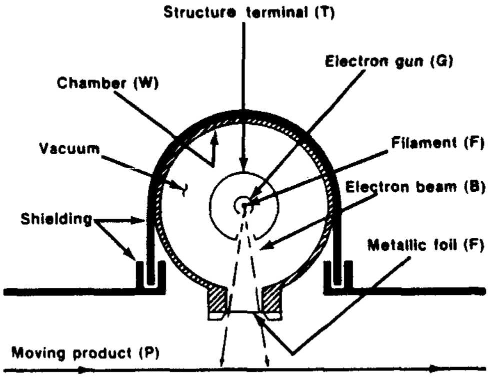
The actual composition of the filaments and their assembly techniques are proprietary to the suppliers of these types of accelerators. Only a few hundred volts are applied to the filament in order to generate the needed electrons.

THE ACCELERATION CHAMBER

The general construction of a low voltage electron beam acceleration chamber is presented below. When positioned in a converting line, this chamber is the most obvious part of the accelerator. It can be around 40 cm in diameter or larger and traverses the entire width of a web.

Electrons are extracted from the filament or cathode (F) by a few hundred volt potential to the electron gun or filament housing (G). This extraction voltage is also used to control the ultimate beam current or the number of electrons emitted in a given period of time. These electrons are then transferred to a concentric terminal (T). A large voltage potential between this terminal (T) and the chamber inner wall (W) is used to accelerate the electrons, the 150,000 to 300,000 volts of the accelerator design and setting. Care is taken in the design of this terminal so that the electrons emitted from it flow toward the metallic foil beam window (F) and are not absorbed in the chamber walls.

Schematic of an Acceleration Chamber



In order to prevent any loss of energy as the electrons are being accelerated, the acceleration chamber is maintained at a vacuum of 10^{-3} to 10^{-4} Pascal. This vacuum also enhances the life expectancy of the filament by reducing the possibility of filament oxidation. A separate vacuum pump and system is supplied with the accelerator.

BEAM WINDOWS

The accelerated stream of electrons seeking ground is directed within the acceleration chamber toward the beam window. This window is a thin gauged (typically 15 micron) titanium foil. Its main function is to maintain the vacuum within the acceleration chamber itself. Being extremely thin, this foil does not absorb much of the electron beam energy and permits most of the accelerated electrons to impinge upon a target or substrate below.

The window, however, does absorb some energy, albeit only a small amount, and does become hot during accelerator operation. Both thermally conductive grids and air cooling are used to keep the beam window near ambient temperatures. In the course of use, the electron beam will actually imprint a burn pattern on the window. To avoid an implosion which could carry materials and unwanted dust into the acceleration chamber, it is good practice to change the beam window as part of a routine preventative maintenance program. The inability to hold vacuum within the acceleration chamber will be indicative of pin holes or of wear in the foil window. Care should also be exercised to see that some of the components of a coating material do not collect on the window over extended periods of time.

The beam window and accelerator filament are the only two components of an electron beam accelerator which require routine replacement. Accelerator manufacturers estimate 10,000 hour service use for a filament under normal production use. The thermal cycling of repeated on and off switching with accelerators used for experimental work will shorten this life expectancy. After more than one year of in service use, it would also be good practice to change the beam window.

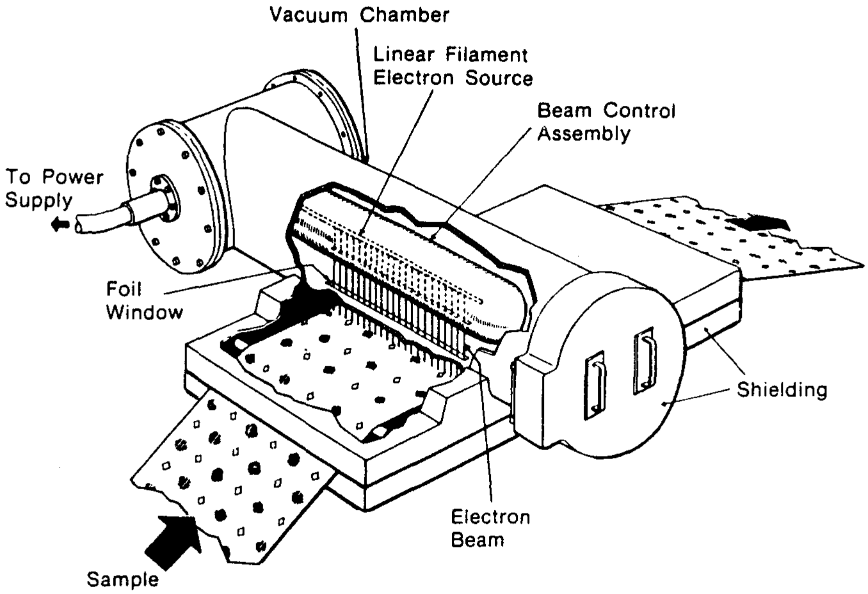
LEAD AND SAFETY SHIELDING

The electrons being emitted by an accelerator flow in a straight line from the beam window toward a target or substrate. When an accelerated electron hits a target material, it can interact with the material and create a desired chemical effect. However, given their high speed and kinetic energy, accelerated electrons may also pass through the target substrate. When an electron hits a target or a material beneath a target it will also generate long penetration X-rays. These X-rays will scatter in every possible direction.

To eliminate any possible worker exposure to such secondary X-rays, the manufacturers of low energy electron beam accelerators encase the critical areas of their equipment in lead. Typically, 2.5 cm (1 inch) of lead is sufficient to stop any X-rays generated by even a 300 KeV accelerator. Such lead casing is used around the entire accelerator chamber itself and around the under beam openings for material transport. The angle and length of such openings are also used to eliminate any possible X-ray emission. Most electron beam accelerators will come equipped with detection devices which will read the background and will be interlocked with the accelerator to shut it down should unwarranted levels of background X-rays be detected.

Lead shielding is practical at the 300 KeV level. At higher acceleration voltages, say above 600 KeV, separate concrete vaults must be constructed in order to eliminate any X-ray emissions. Thus, these 150 KeV to 300 KeV accelerators are often called self-shielded.

Self-Shielded Electron Beam Accelerator



In addition to guarding against X-ray emissions, due consideration is given to the design of under beam transport systems and the area directly under the beam. When the stream of electrons emitted by an accelerator is absorbed in a target, heat is also generated. Thus, care is taken to see that the area immediately under the beam is cooled. In most situations, a water cooled metal plate is positioned directly below the beam. When drum curing is being used, the drum beneath the beam is also water-cooled. In situations in which an inert gas atmosphere is introduced in order to enhance the reaction rate of a material exposed to electrons, the inert gas itself can serve as a coolant to cool the open space beneath the beam.

SYSTEMS CONTROLS

In general, the voltage of an electron beam accelerator is set during the design and construction of the unit. Most accelerator manufacturers provide a voltage step down feature which permits operating the accelerator at less than the maximum rated voltage. Thus an accelerator capable of delivering 300 KeV electrons can, with a simple adjustment of a dial setting, be turned down to deliver lower voltage electrons. Therefore, there is a lower total power consumption which permits more economic conversion of thinner gauged materials. 300 KeV electrons, which can effectively penetrate 0.4 mm (15.7 mils) of unit density material need not be used if 0.2 mm (7.9 mils) of penetration, which can be generated from only 200 KeV, is sufficient to thoroughly cure a given material. Some work has been done using two low voltage accelerators to irradiate webs from both sides. Because of the combined integration of two depth versus dose curves, 2.4 times the effective beam penetration of a single accelerator can be achieved. Thus, two cross-fired 300KeV self-shielded accelerators can be used to penetrate and cure webs of nearly 1.0 mm (40 mils) in gauge thickness.

DOSIMETRY

The exposure of a target material to an electron beam is often called the dose. Dose is most often expressed in megarads wherein one rad equals 100 ergs per gram of absorbed energy. A megarad (Mrad or MR) is therefore 10^8 ergs per gram or 10 Joules of energy. The conversion of most coatings, inks and adhesives requires dose exposure of between one and three megarads to exhibit full cure. One megarad is also equal to 10 Joules per gram exposure or 10 kiloGrays, the Gray being a newer international unit of dosimetry with one Gray being equal to 100 rads. In contrast to electron beam exposure, ultraviolet exposure is often in the range of 0.1 to 0.5 Joules. Because of differences in web speeds and lamp intensity versus beam currents, it is difficult to establish any specific correlation between the exposure dose under an electron beam and that under a system of ultraviolet lamps.

DOSIMETRY RELATIONSHIPS

Dose = energy absorbed per unit mass.
Rad = unit of dose equal to the absorption of 100 ergs per gram.
Megarad = MR or MRad = 1 x 10^6 rads = 10 KiloGrays = 10 Joules per gram = 2.39 calories per gram = 4.3 BTU per pound = 10 Watt-seconds per gram = 4.54 kW- seconds per pound.
Gray = unit of dose = absorption of 100 rads = 1 x 10^4 ergs per gram.
KiloGray = 1,000 Grays = 0.1 megarads = 1 Joule per gram.
1 Megarad = 1 x 10^8 ergs per gram absorbed energy = 10 KiloGrays.

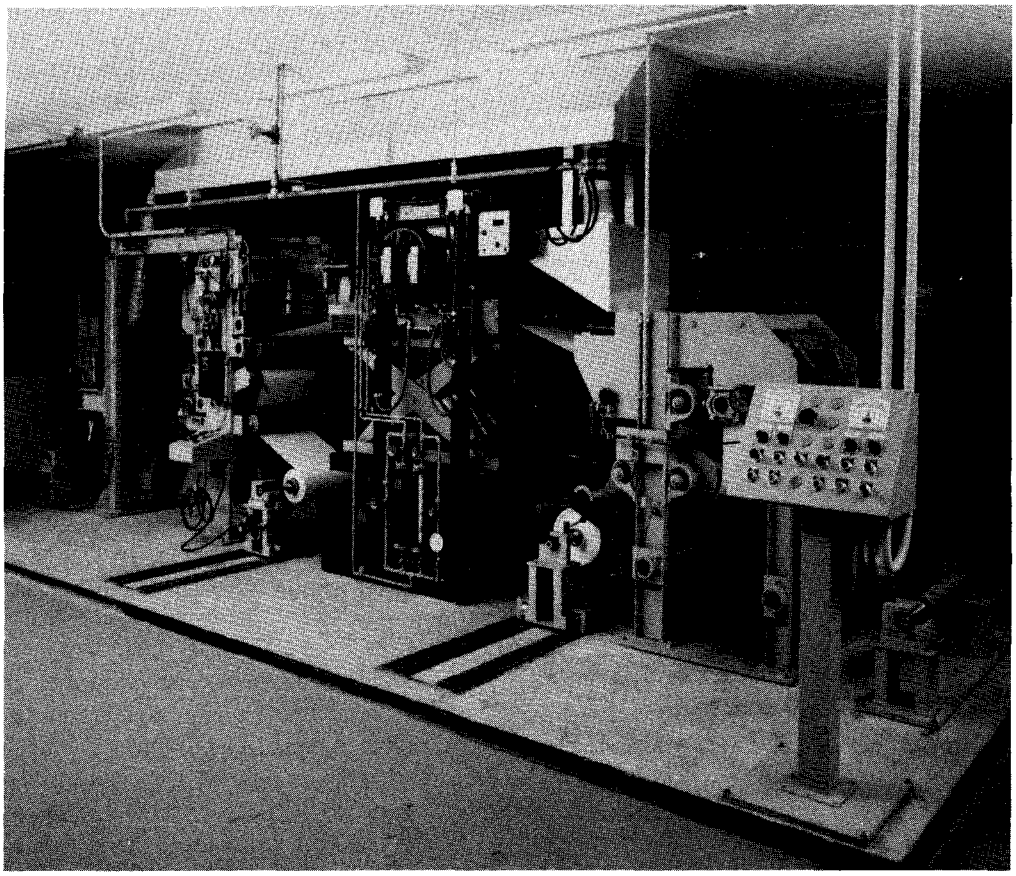
In actual practice one can choose to ignore this highly technical concept and operate an accelerator strictly by controlling line speed and beam current. The relationship between the line speed of a moving web and the beam current dictates the electron beam exposure level. For any given material, there is an optimum relationship between these two operator controllable parameters which will assure the desired state of cure. Being a completely electrical device, the beam current of an electron beam accelerator can be slaved to or electrically interlocked with the drive systems for under beam transport. Thus, any increase in web speed would result in a corresponding and appropriate increase in beam current, keeping the substrate exposure level constant. Likewise, beam current and line speed can be reduced with the same fixed ratios. This permits the minimum use of materials during start-ups and shut downs. The equation below shows that accelerator current and line speed are directly proportional.

$$\text{Dose} = \frac{\text{k x I}}{\text{line speed}}$$

Where dose is expressed in megarads, I is the beam current in milliamps, line speed is in meters per minute and k is an empirically derived proportionality constant based upon the line width and geometry and the distance of the product from the beam window.

Obviously, in relying on linear cathodes, electron beams are suited for use with flat sheet or web fed materials. Because of the need to maintain vacuum in the acceleration chamber and the consequent use of a foil window, complex beam configurations are not possible. This does not necessarily preclude the use of electron beams with three dimensional objects. Sophisticated under beam transport devices have been developed which permit the controlled rotation of objects under the beam, especially if they are transported down the length of the beam window.

An Electron Beam Accelerator Installed on a Web Curing Line



By the end of the 1980s, over 120 low energy (300 KeV or less), self-shielded electron beam accelerators were installed on production lines throughout the world. More than 200 such units exist as laboratory or pilot units. Units have been made which can accommodate web widths as wide as 2.4 meters (nearly 8 feet) and lines speeds as high as 1,500 meters per minute (in excess of 4,900 feet per minute). More commonly, low energy electron beam accelerators are used in production situations capable of running at web process speeds on the order of 700 meters per minute (nearly 2,300 feet per minute).

ULTRAVIOLET VERSUS ELECTRON BEAM CURING

In most instances, ultraviolet light and electron beam radiation curing do not compete directly with each other. Ultraviolet light curing systems are more suited for narrower web operations and for processes in which short run situations arise, such as in some printing operations. Electron beam curing can handle thicker and more dense or opaque materials and do so at very high processing speeds. The capital costs for these two types of radiation curing equipment differ significantly. A production sized electron beam accelerator can cost in the order of $500,000 or more, depending on the degree of customization demanded by a potential user. Ultraviolet systems can range from small production units of several tens of thousands of dollars to large scale units in the hundreds of thousands of dollars league. A concern of some considering electron beam curing is not the reliability of the process and sometimes not even the cost of the capital equipment, the accelerator, but the ability of the firm to sell and market the high quantity of output one can achieve with electron beam curing. Many firms prefer the versatility that multiple ultraviolet curing lines give them.

Chapter Four

CHEMISTRY

INTRODUCTION

Monomers are the simplest building blocks from which synthetic organic materials are made. A simple monomer derived from petroleum feed is ethylene. This is represented by:

$H_2C = CH_2$

The symbol "=" between the two units or atoms of carbon represents a reactive site or, as chemists refer to it, a double bond or unsaturation. It is sites like this which react to form bigger or larger chemical materials called oligomers and polymers. A polymer is a grouping of many (i.e. poly-) repeat units of the same monomer. The term oligomer is a special term used to designate those polymers which are not that large and which often can be further reacted to form a large combination of polymers. For example, ethylene can be combined to form poly-ethylene:

$-(CH_2\text{-}CH_2)\text{-}(CH_2\text{-}CH_2)\text{-}(CH_2\text{-}CH_2)\text{-}\ldots(CH_2\text{-}CH_2)\text{-}(CH_2\text{-}CH_2)-$

The lack of double bonds indicates the polymer is saturated.

By itself, ethylene exists as a gas. When ethylene monomer is combined to form polyethylene, a tough strong plastic results. Because of its lack of unsaturation or double bonds, polyethylene is very inert and resistant to environmental attack. When considered as a distinct chemical unit, either as a monomer or as a polymer chain, the chemically linked units of carbon and hydrogen are called molecules. Since each element has a measurable relative weight, both the monomer and its polymer can be considered to have molecular weights. With hydrogen having and atomic weight of 1 and carbon an atomic weight of 12, the ethylene monomer, $H_2C = CH_2$, would have a molecular weight of 28. For polyethylene, the molecular weight would depend upon the number of repeat units of ethylene which are combined to form its structure. Commercial polyethylenes used for films or molded goods typically have molecular weights in the order of 100,000.

UV/EB CURABLE MATERIALS

Ultraviolet and electron beam processing involves the polymerization of monomers and oligomers directly on the substrate. This polymerization occurs at a very high rate when the coating, ink or adhesive is exposed to either ultraviolet light or an electron beam. The polymerization rate depends upon the intensity of the radiation used. This ability to control or time the cure process enables one to have a shelf stable, one package, high solids system which cures rapidly at room temperature.

Commercial applications for these materials include coatings, inks and adhesives. These products are complex mixtures of oligomers, monomers and additives.

A complete formulation for a coating, ink or adhesive consists of a blend or mixture of:

- the base oligomer which imparts most of the basic properties to the final cured or crosslinked material.
- the monofunctional monomers which dilute the formulation to the suitable application viscosity.
- the multifunctional monomers which help form the crosslinks between segments of the oligomer.
- specialized additives used to impart specific properties.
- pigment, for inks and some coatings.
- photoinitiators for UV systems which, as the name implies, convert the energy from light into either free radicals or cations which start the polymerization.

It is the task of the formulator to judiciously choose the appropriate base materials for use in a system which can be easily handled during application, can be responsive to the radiant energy, and can provide the desired properties in the finished product. Thus, it is important to discuss each of these classes of materials in detail.

Oligomers

The overall properties of any coating, ink or adhesive to be crosslinked by radiant energy are determined primarily by the oligomer used in the formulation. Oligomers are moderately low molecular weight polymers which have been specially designed to impart a desired set of properties. Oligomers vary in molecular weight from around 400 to 7,000. While the lower molecular weight materials are pourable liquids, the higher molecular weight oligomers are quite viscous. Moderate heating is useful in handling these more viscous oligomers when formulating or when using these materials in manufacture.

Most of the commercially available oligomers used in radiation curable formulations are based on the acrylation of different chemical structures. The acrylation process imparts the unsaturation or the (C=C) group to the two ends of the oligomer. In essence then, most oligomers can be viewed as difunctional entities. The structures most commonly found are:

1. acrylated urethanes
2. acrylated epoxies
3. acrylated polyesters
4. acrylated silicones

The final properties of a fully cured or crosslinked coating, ink or adhesive depend upon the interaction of all the materials in the formulation; however, the oligomer contributes substantially to these properties. Each class or type of acrylated oligomer imparts specific properties to the product.

Acrylated urethanes crosslink into tough, flexible materials which exhibit good abrasion resistance. These oligomers are formulated into printing inks and abrasion resistant top coats for use as overprint varnishes and mar resistant coatings on wood surfaces and vinyl flooring.

Acrylated epoxies convert into somewhat harder materials which are more useful as coatings or adhesives on rigid substrates such as metal cans and paneling or as binders in composites. The epoxy structure itself tends to contribute to adhesion on nonporous substrates as well as enhancing chemical resistance.

Acrylated polyesters can produce coatings or adhesives with properties dominated by the polyester structure used in forming the oligomer. Soft, pressure sensitive adhesives have been made from acrylated polyesters. Likewise, strong, rigid adhesives for bonding metal-to-metal have also been made from polyester oligomers.

Acrylated silicones represent some truly novel materials which have to date found use as release coatings on papers and films; however, one can envision even broader uses for materials which would have the well known thermal and age resistance of silicones in general.

A wide variety of pure acrylic oligomer formulations have been made which are responsive to radiant energy. Such materials are often used as adhesives for bonding components together. Point sources of ultraviolet light facilitate this technique.

In addition, other oligomers or low molecular weight polymers which have reactive double bonds (C=C) in their structure can be used to modify these oligomeric systems or used by themselves. For example, butadiene-acrylonitrile oligomers, which on their own crosslink into rubbery materials, have been shown to flexibilize epoxy acrylate systems. 1,2-Polybutadiene oligomers, in which the C=C group is pendant to the oligomer backbone, are also non-acrylate materials which can form flexible coatings after being subjected to radiant energy.

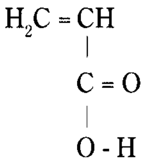
Monomers

Monofunctional monomers have only one reactive group, most commonly a double bond (=) or unsaturated structure. This permits the monomer to react when exposed to radiant energy and to become incorporated into the cured or finished material. In formulations, monofunctional monomers are primarily used as diluents to lower the viscosity of the system. The required end use properties of a coating or adhesive may call for the use of a certain type of oligomer. When used in a formulation, some oligomers may be too viscous to be efficiently handled in a given process or on certain application equipment. Thus, one dilutes these systems with monofunctional monomers which can both lower the viscosity and react into the finished product.

Besides serving as diluents, monofunctional monomers can also affect the properties of the cured coating, ink or adhesive. The specific chemical structure of these monomers will govern their ability to promote adhesion to nonporous substrates, to harden or flexibilize the cured material, or to add some unique properties to the finished product. Because one is dealing with monomeric or relatively low molecular weight materials, care must be exercised to see that the quantity and type of monomer chosen for use in a formulation does not pose volatility or worker exposure problems. In general, the lower the molecular weight of a specific monomer, the higher its vapor pressure or tendency to volatilize or evaporate. Bear in mind, that there is some small heat build-up when a material is exposed to radiant energy as ultraviolet light.

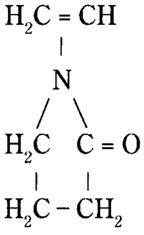
Some commonly used monomeric diluents are:

Acrylic acid:
- used as an adhesion promotor

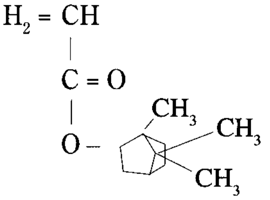


$$H_2C=CH-C(=O)-O-H$$

N - vinyl - 2 - pyrrolidone:

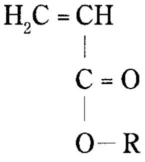


Isobormyl acrylate:



Other monofunctional diluents have been used. These are generally based on acrylic acid derivatives. Different substituent groups (R) are used to impart certain properties and/or enhance the compatibility of the monofunctional monomer with specific oligomers.

Monofunctional acrylates:



$$H_2C=CH-C(=O)-O-R$$

Multifunctional Monomers

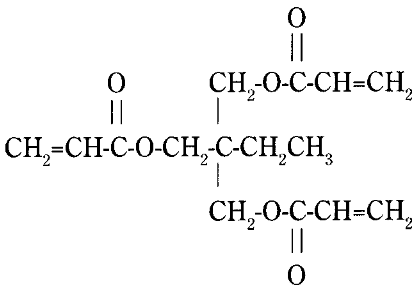
Although they are still relatively low in viscosity and function as diluents to reduce the viscosity of a formulation, multifunctional monomers serve a more important purpose. The functional properties of a coating, ink or adhesive depend on converting formulations which are applied as liquids, albeit sometimes viscous, to solids or more firm materials. The chemical process by which this takes place is called crosslinking. Multifunctional monomers serve to form the links between oligomer molecules and other monomers within a formulation.

If one envisions an oligomer molecule as a tiny segment of a string, one can grow or create a bigger molecule by tying together the ends of different strands of string. Chemists call this chain extension; however, these longer molecule chains might still be relatively weak and would probably not exhibit all of the desired finished properties. By creating links between various strands, like forming a net, properties like hardness, toughness and strength can be developed.

In coating, ink or adhesive formulations, multifunctional monomers create these crosslinks. An indication of having achieved a crosslinked state is the lack of solubility of the material in a good solvent for its base ingredients. The relative degree of swell in such a solvent system will indicate the tightness or relative degree of cure or crosslinking achieved. The tighter the crosslinks (the smaller the interstices of the net), the less the volume swell in the appropriate solvent.

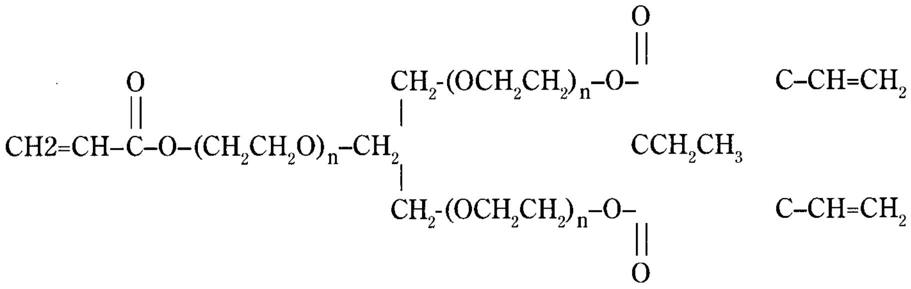
Some commonly used multifunctional monomers and their ethoxylated derivatives are:

Trimethylolpropane triacrylate (TMPTA):



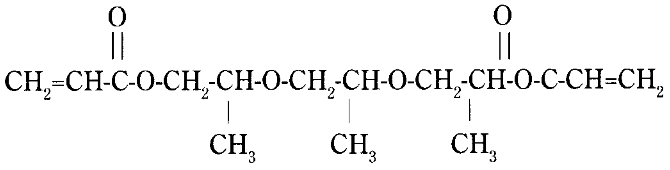
$$CH_2=CH-C(=O)-O-CH_2-C(CH_2-O-C(=O)-CH=CH_2)_2-CH_2CH_3$$

Trimethylolpropane ethoxylate triacrylate (TMPEOTA)



$$CH_2=CH-C(=O)-O-(CH_2CH_2O)_n-CH_2-C(CH_2-(OCH_2CH_2)_n-O-C(=O)-CH=CH_2)_2-CH_2CH_3$$

Tripropylene glycol diacrylate (TPGDA):



$$CH_2=CH-C(=O)-O-CH_2-CH(CH_3)-O-CH_2-CH(CH_3)-O-CH_2-CH(CH_3)-O-C(=O)-CH=CH_2$$

Obviously, a tri- or tetra-functional multifunctional monomer will form a much tighter crosslinked network than a difunctional one; however, with difunctional acrylates there is a greater degree of latitude in selecting the specific chemical make up of the hydrocarbon units between the terminal reactive acrylate groups. This is most important when dealing with the compatibility of the multifunctional monomer and the oligomer used in a formulation.

Additives

Coatings, inks and adhesives intended to be cured by ultraviolet or electron beam energy contain additives typically used by these types of products regardless of the mechanism of cure. For UV cured systems, one needs to minimize the absorption of light by additives in the frequency range needed to initiate the polymerization. Typical additives are:

- pigments
- fillers
- defoamers
- adhesion promotors
- flatting agents
- wetting agents
- slip aids
- stabilizers

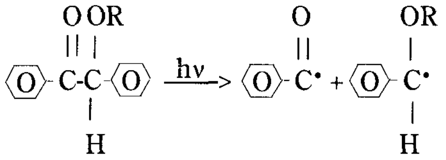
The crosslinked coatings, ink and adhesives are still organic materials. In order to retard their degradation from severe environmental attack by oxygen or other predators, small amounts (1 percent to 2 percent) of very specialized materials, such as antioxidants or fungicides, are incorporated into the formulation, especially where long term outdoor exposure is anticipated. With filled or pigmented systems, wetting agents are used to promote the dispersion of these ingredients. In some cases, specific reactive monomers or similar additives are used to enhance the adhesion to nonporous substrates. Again, it is the expertise of the formulator which guides the selection and balance of these additives.

When developing pigmented formulations, attention must be paid to the type of energy which will be used to convert the material. Photons of ultraviolet light tend to be absorbed on the surface being exposed. Electrons, on the other hand, have the capability of penetrating through matter irrespective of its density. Thus, a very opaque white base coating containing titanium dioxide, will cure completely through when exposed to electrons, but may not exhibit total through cure when exposed to ultraviolet light. Other opaque materials, like coatings filled with aluminum flake and magnetic iron oxides, may also require electron beam curing.

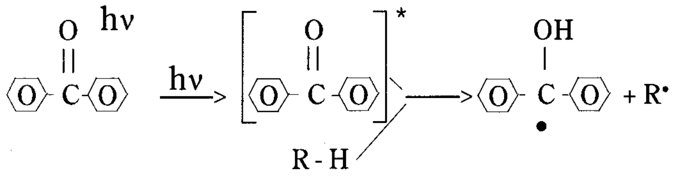
Translucent fillers, the pigment types, and loadings used in the primary colors for three or four color printing are used in coatings and inks which can be crosslinked by ultraviolet light. The amount of the coating or ink applied to a substrate is so thin that the light energy can still activate its curing mechanism; however, because of the different degree of ultraviolet absorption exhibited by each color, the formulator must make slight adjustments in the amount of photoactive initiator used in each system.

Photoinitiators

Photoinitiators absorb light and are directly involved in the production of free radicals or cations. There are two main classes of photoinitiators in free radical systems, photocleavage initiators and photo-abstraction initiators. Typical photocleavage initiators are benzoin ethers which generate free radicals by the following mechanism:



The most common hydrogen-abstraction initiator is benzophenone which generates free radicals by the following mechanism:



The hydrogen donor radical initiates free radical polymerization. Tertiary amines are very effective hydrogen donors and are often used along with benzophenone.

Cationic photoinitiators generate very strong Bronsted acids on exposure to ultraviolet light. The most commonly used initiators are triarylsulfonium or diaryliodoniom salts. The mechanism for acid generation is illustrated below:

$$Ar_3S^+X^- + RH \xrightarrow{h\nu} Ar_2S + Ar^\bullet + R^\bullet + HX$$

Cationic cure will be described in more detail in a following section of this chapter.

POLYMERIZATION (CURE)

On exposure to light or an electron beam the coating, ink, or adhesive undergoes polymerization. The polymerization reaction converts the liquid material into the cured product. The two types of polymerization used in radiation curing are free radical and cationic.

FREE RADICAL CURING

Free radical polymerization contains the following steps:

Initiation $R \xrightarrow[\text{electrons}]{\text{UV or}} R^\bullet$

Propagation $R^\bullet + R_1 \longrightarrow RR^\bullet_1$

Chain Transfer $RR^\bullet_n + AH \longrightarrow RR_nH + A^\bullet$

Termination $R_n^\bullet + R^\bullet_m \longrightarrow R_nR_m$

Initiation

The use of radiation provides very fast and controlled generation of highly reactive chemical species which initiate polymerization. Most of the advantages of UV/EB curing result from the high degree of control over the initiation process.

The major difference between ultraviolet light and electron beams is in the initiation process. Electrons can penetrate matter and transport sufficient energy to interact directly with the atoms in a molecule generating the free radicals. As a result high energy electrons can directly initiate polymerization.

Ultraviolet light, on the other hand, does not transport sufficient energy to directly generate free radicals with just monomers and oligomers. Photoinitiators are used to absorb the light energy and generate the free radicals. These initiators are added in the range of 1–8 percent of the formulation. The exact initiator content must be precisely defined for each formulation. Unlike the use of some historic additives in air drying or oxidative systems, such as the driers used in printing inks, adding more photoinitiator to a system may not enhance its response to ultraviolet light and can even be detrimental.

A consequence of the difference between EB and UV initiation is that EB can cure heavily pigmented systems and thicker films, while in UV light cured products, the rate of cure is adversely affected by pigments and thickness.

Propagation

After initiation, the conversion of the product into a cured solid material proceeds as a normal bulk free radical polymerization.

The initiation process occurs only during exposure of the material to EB or UV energy. Since any existing free radicals have very short life spans, all of the propagation reactions also stop when the material is no longer under the source. Consequently, the final product's properties are achieved immediately after removal from the energy source. Since exposure times are generally in fractions of a second, one can see how fast and efficient production rates can be attained with these forms of energy.

Termination

Free radical polymerization can be retarded and even terminated by the presence of oxygen. One common way to overcome this problem is to use an inert gas in the space beneath the electron beam window or in front of the ultraviolet sources. Nitrogen gas has been found to be an industrially viable inerting material. Some work has also shown that carbon dioxide, which is produced as a combustion by-product from burning heating oil, can also be used.

With ultraviolet light activated systems, the use of the hydrogen abstraction photoinitiators with tertiary amines or the use of cationic chemistry (see below) tends to be less sensitive to inhibition or termination by the presence of oxygen. The effect of oxygen on the curing of a given material must be determined in each case and in consultation with the coating, ink or adhesive supplier.

Other termination reactions involve the growing polymer sites reacting together as illustrated by:

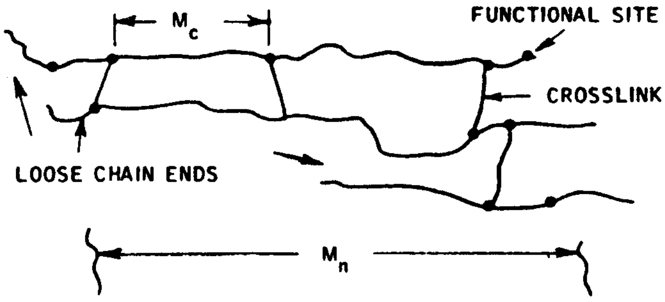
$$R^{\bullet}_{n} + R^{\bullet}_{m} \longrightarrow R_{n}R_{m}$$

MOLECULAR WEIGHT BETWEEN CROSSLINKS

The properties of formulations which have been converted or crosslinked by UV/EB energy can be characterized by conventional test methods used in a given industry. Hardness, flexibility, and resistance tests as well as tensile and elongation properties can be run on coatings. Color fastness, rub resistance and other graphic arts tests can be run on inks cured with radiant energy. Likewise, bond strength and durability tests can be used to evaluate the radiant energy crosslinked adhesives. Consult *Radiation Curing Test Methods,* published by RadTech International, for suitable test methods.

In order to understand how some of these parameters are affected by the choice of formulating variables and the exposure level to the radiation, one can also examine the average molecular weight between crosslinks (M_c). This will give insight into such problem areas as shrinkage during cure and the flexibility or elongation of the cured material. An illustration of a crosslinked network is:

Crosslinked Polymer Network



The hardness and the glass transition temperature of the cured film are functions of both the crosslink density and the polymer backbone of the network making up the cured film. For the same type of polymer, epoxy for example, hardness, glass transition temperature and solvent resistance increase with increased crosslink density, or as M_c decreases. Reducing the crosslink density, however, improves the properties of flexibility and elongation.

Crosslink density is influenced by the molecular weight and functionality of the starting raw materials as well as the degree of cure.

CATIONIC CURING

Besides the free radical chemistry discussed above, there are other systems which also avail themselves to the use of UV/EB processing.

Ultraviolet light is capable of activating a unique class of photoinitiators which can in turn propagate a crosslinking reaction via an ionic rather than via a free radical mechanism. Because this is a fundamentally different chemical mechanism, different reactants, such as the oligomers and monomers, are required. This chemistry does not function with the type of double bonds or unsaturation found in the oligomers and monomers discussed earlier.

Cationic photoinitiators are generally arylsulfonium salts, which upon exposure to ultraviolet light can decompose to yield an acid catalyst. These salts often consist of complex aromatic-sulfur structures with non-nucleophilic anions.

Epoxy resins are the most common resins used in cationic curing. Saturated cycloaliphatic epoxies have been used most widely because of their high rate of cure and proven environmental resistance. Hydroxyl groups cure with epoxies during cationic polymerization. Therefore, all of the polyols developed for urethanes are available as formulating ingredients. Low molecular weight divinyl ethers have been found to be effective diluents which cure quickly and can add flexibility. Vinyl ether based oligomers have recently been developed, allowing for the formulation of all vinyl ether coatings, inks or adhesives.

Unlike free radical systems, cationic polymerization continues to propagate after the removal of the radiation source. As a result, cationic systems have been found to develop better through cure than free radical systems. One can also expose a film to very low levels of energy and then bake the coating to finish the polymerization. Cationic cure of epoxies occurs through a ring opening process which creates minimal shrinkage. Oxygen does not inhibit cationic polymerization. Reaction rates may be increased by preheating with IR lamps or by eliminating high humidity with dry air purges.

Some of the end use applications for materials cured with cationic technology are protective coatings for metals, such as can ends, printing inks for use on metals, and specialty adhesive and sealant systems. Because of the through cure capabilities, cationic systems are also used for the potting and encapsulation of electronic components. Studies have indicated no trace of the catalytic acidity once cure is complete. Superior resolution in stereolithography has been achieved with cationic oligomers.

HYBRID SYSTEMS

UV/EB curable systems are not always liquid 100 percent reactive materials. Coatings and adhesives that are applied as emulsions or with solvent are commercially available. Special water dispersable photoinitiators have been developed for use with emulsions. Mixtures of free radical and cationic materials may be cured to incorporate desirable properties from both systems. Electron beam crosslinking has also been used with melt applied adhesives. Special styrene-isoprene-styrene block copolymers have been developed which can be electron beam crosslinked to enhance the thermal resistance of a melt deposited coating. High temperature resistant pressure sensitive adhesive tapes have been made in this way.

Another hybrid technology is to use ultraviolet or electron beam curable materials in conjunction with materials which rely on other crosslinking mechanisms. For example, dual cures involving the use of radiant energy to crosslink one polymer phase have been combined with traditional two component cure technology to produce coatings which have superior resistance to environmental attack. These systems can involve acrylated oligomers and traditional two component polyurethanes. In addition, thermally activated cure or bake cycles can be used to cross-link some materials not responsive to ultraviolet or electron beam energy. Such bake cycles can enhance the toughness of some cationic cured coatings used on metals.

The possibilities for these hybrid or dual cure systems are endless. They permit the use of the efficiency and economics of high speed radiant energy processing along with more traditional methods of application or curing.

EFFECTS ON HIGH POLYMERS

The substrates used in many coating, graphic arts and adhesives applications are often high polymers. Sometimes these can be made from naturally occurring materials like paper and wood products. Other times they can be made from high molecular weight synthetic polymers. Different effects can be observed depending on the type of energy used in a given application.

Of main concern, with the use of ultraviolet energy is the effect of the heat output from most lamp sources upon the substrate. Care must be given to the handling of very flexible or soft plastic films. Black materials will be highly absorbent of the heat energy or infrared output from an ultraviolet source.

Electron beams present different concerns because of the capability of the electrons to penetrate matter. Organic materials tend to have three different types of response to electron bombardment depending upon their own chemical composition. Some high polymers, such as polyethylenes and some synthetic rubbers, will crosslink under electron beam radiation. Such crosslinking is often used with polyethylene to enhance its functioning at elevated temperatures by increasing its melt temperature. Some high polymers, such as polypropylenes and polytetrafluoroethylenes, will break down or scission when exposed to electrons. There are, however, specialty polypropylene grades which can withstand the relatively low levels of electron exposure used in converting coatings, inks and adhesives. Finally, there are a number of synthetic polymers which will be relatively unaffected by electron beam exposure. These tend to be materials which have aromatic chemical structures. Polyester films and specialty high temperature thermoplastics are of this type.

When dealing with electron beam crosslinking, some concern must also be given to the possible effects on substrates. Unlike processes such as the corona discharge treatment of plastic substrates, electron beams by themselves are not known to enhance surface bondability.

Chapter Five

HEALTH AND SAFETY

INTRODUCTION

Over the past decade, there has been a rapid increase in the use of various radiation sources for a variety of purposes, including lasers, light emitting diodes and medical research devices. Of particular interest in the ultraviolet and electron beam processing industry is the use of energy to cause electronic excitation of molecules causing the polymerization reaction to occur. As with most industrial processes, there are many advantages attributable to UV/EB processing, but there are also hazards. These hazards are attributable to the reactive chemicals and solvents used in the inks, coatings and adhesives, as well as the energy sources and their potential by-products.

Ultraviolet curing processes utilize a form of electromagnetic radiation called actinic, or nonionizing radiation. Ultraviolet energy is not sufficient to penetrate into the body and interact with the tissues to cause dramatic effects, such as cancer, which are associated with other forms of radiation. It is well known that ultraviolet rays from the sun have an effect on both the skin and eyes, as does direct exposure to an ultraviolet lamp.

Electron beam processors are capable of generating ionizing radiation when they are in use and therefore they are shielded and also have fail-safe interlocks to protect employees. This ionizing energy includes X-rays, gamma rays and the high speed electrons needed to cure the ink, coating or adhesive.

Another concern with UV/EB curable systems, as with any chemicals, is the hazards associated with the materials used to formulate these systems. The purpose of this chapter is to introduce the necessary terminology in the occupational health field, the hazards associated with these processes, the method of hazard communication, and the ways to protect workers from the hazards.

IMPLICATIONS OF TOXICOLOGY AND INDUSTRIAL HYGIENE

Before proceeding to discuss the safety of radiation curing, it is necessary to define key terms from the field of occupational health, the first of which is *toxicology*.

Toxicology refers to the collection of disciplines which study the biological effects of chemicals, products and processes in man, animals, plants and the lower organisms.

A related, and perhaps more relevant term, which is important to the understanding of UV/EB curable systems, is that of *toxicity*. Toxicity is the ability of a substance to cause injury to a living organism, but it cannot be defined without referencing exposure dose, method of exposure, frequency of exposure, type and severity of the injury, and the time needed to cause injury. This leads to the next term, *hazard*, which is the likelihood that a substance will cause injury under a given set of conditions of manufacturing, use or disposal. The two concepts can be related by noting that some very toxic materials can present minimal hazards when they are used in well-controlled environments and therefore employee exposure is minimal. These concepts were summarized by the scholar Paracelsus who centuries ago wrote the phrase which is still valid today, "Only the dose makes the poison." Any substance, including water, can be hazardous.

Industrial hygiene is the science of protecting human health through the control of the work environment. It involves the application of biological, chemical, physical and engineering science to recognize, evaluate and control potential or existing manufacturing work conditions which may cause worker discomfort, inefficiency or injury. The principles of recognition, evaluation and control apply to employee exposures to both chemical and physical agents.

The last item which requires definition is really a process. This process is *hazard communication* or *right-to-know*. While this process exists in many forms, including the Federal Hazard Communication Standard and various state, federal and local laws, the basic components are similar. The components are product warning labels, material safety data sheets (MSDS) and worker education and training.

The importance and interaction of all three components as necessary to protect the employee cannot be stressed too strongly.

Product labels are usually the first source of information the worker sees regarding the hazards of a material. If the labels are written in accordance with the OSHA hazard communication standard requirements, the language can be very threatening. At a minimum, a proper product label for hazardous chemicals requires the following be included:

- Identity of the hazardous chemical — this includes any chemical or common name which is on the MSDS and permits easy cross referencing.
- Appropriate hazard warnings — these must convey specific types of physical and health hazards (target organ warnings) associated with the chemical or mixture of chemicals.
- Name and address of the chemical manufacturer, importer or other responsible party.

Per 29CFR 1910. 1200 (f) a second, more detailed hazard communication document is the material safety data sheet, or MSDS. OSHA's hazard communication standard sets the following minimum requirements for the material safety data sheet:

- Identity — to permit cross referencing to the label
- Ingredients — the chemical and common names of all materials which contribute to the hazards of an untested mixture when they are present at levels greater than:
  - 1.0% for health and physical hazards
  - 0.1% for carcinogenic materials
- Physical and chemical characteristics

- Physical hazards including the potential for fire, explosion and reactivity.
- Health hazards, including signs and symptoms of exposure and medical conditions which could be aggravated by exposure and primary routes of entry
- Workplace exposure limits
- Carcinogenicity
- Precautions for safe handling
- Applicable control measures
- Emergency and first aid procedures
- Date of preparation of the MSDS
- Name, address and phone number of preparer

MSDS are to be sent to all purchasers of a hazardous chemical with the first shipment and when the composition changes or new information becomes available. The MSDS must be readily available to all employees.

With the requirements just discussed and the complexity of the labels and MSDS it is important that the workers be trained to understand these documents and to use the materials they describe properly. The best time for training is when the installation of the new curing equipment is complete and start-up is imminent. Many manufacturers of the inks, coatings and adhesives will not only provide the labels and MSDS, but also assist with on-site training of the workers. This training not only discusses the information on the labels and MSDS, but also should include an explanation of safe handling procedures which have been established by the appropriate professional.

CHEMICAL HAZARDS

The materials used in UV/EB curable systems present hazards for skin and eye contact, possibly a hazard from accidental ingestion and, to a lesser extent (at least historically), from breathing materials which are volatilized during processing. This latter concept is currently in a state of change due to the introduction of three-dimensional ultraviolet curing, where the coatings are spray applied and are formulated similar to classical coatings in that they contain organic solvents and may also contain reactive, volatile diluents such as styrene. For the acrylate-type of chemicals used, some are corrosive to the eyes and skin, all are at least irritating to some degree, and many may cause an allergic type of dermititis. A limited number of monomers have caused several types of cancer in laboratory animals after long-term skin painting studies.

Many installations where UV/EB curable materials are used have experienced some problems with skin effects shortly after installation and before proper handling procedures are implemented and enforced. Therefore, it is important to implement proper handling procedures from the first day of operation. The systems can cause a variety of effects on the skin, the exact classification of which is difficult. Most generically classified occupational dermatitis is caused by primary irritant chemicals, a class into which acrylates fit. Agents such as these cause dermatitis by direct action on normal skin at the site of contact if they are present in sufficient intensity or quantity for a sufficient length of time. Thus, most people will react to primary irritants if the above requirements are met. Strong irritants, such as acids or caustics produce an observable effect with only a few minutes of exposure, while weak or marginal irritants may require several days to develop a response.

Occupational contact dermatitis is a general term describing many effects upon the skin. It is estimated that about 20 percent of occupational dermatitis is caused by allergenic materials, a class in which most acrylated radiation curable materials are grouped. Skin sensitizers differ from primary irritants in the mode of action and in the effects they create within the skin. Most sensitizers do not produce demonstrable changes on the first contact or perhaps after many days or weeks of exposure; however, the sensitizer induces specific changes in the skin so that, after an incubation period, further contact with the material, or a closely related material on the same part or other parts of the body results in an acute skin reaction. While it is difficult for an occupational physician to separate the causal factors between a primary irritation and allergenic sensitization, a practical difference is that an irritant usually affects a majority of people overexposed to the agent, while a sensitizer generally affects only a few.

There is one additional category of acute skin effects into which UV/EB curable materials fit. Many of these materials are also classified as photosensitizers, since they have the ability to increase an exposed person's susceptibility to reaction to light. In simplest terms this means that these materials left on the skin and subsequently exposed to sunlight may result in a sunburn. Photosensitizers can also be described as phototoxic and photoallergic, two terms which are analogous to the previous discussion on primary irritants and allergic sensitizers.

The final important effect on the skin (or, in a few cases, internal organs) is that of carcinogenicity. Many radiation curable monomers have been tested in long-term animal skin painting studies for their ability to induce tumors. A few of the materials tested have produced positive results in these tests. While cancer is often viewed as a dramatic effect, two very important points should be noted. The first is that no excesses in cancer have been observed in workers with long-term exposure during the manufacture of these materials, and more importantly from a processor standpoint, it should be obvious from the previous discussion on other skin effects that employees must be protected from skin exposure. Therefore, if the skin is protected so that irritation and sensitization do not occur, then the chances of developing cancer are minimized or eliminated.

Given the effect of this class of chemicals on the skin, it is not surprising that they can also produce dramatic effects on the sensitive tissues of the eyes. They can cause contact irritation similar to the effects on the skin.

Until the recent development of three-dimensional UV curing technology, inhalation exposures in the UV processing industry were generally not thought to be significant. This is primarily due to the rapid curing mechanism, the method(s) of application and the very low volatility of the materials. If anything, the acrylate-type of materials possess a unique odor and to those unfamiliar with the odor, this factor is often the most problematic in start-up.

With the three-dimensional curing systems, both volatile reactive diluents, such as styrene and organic solvents, may be used to reduce the viscosity to the level required for application. Also the method of application will most often be with spray equipment. Fortunately, control technologies and methods are available for the materials being considered for use in these systems. This exposure assessment is part of industrial hygiene.

PHYSICAL AND PROCESS HAZARDS OF UV

Ultraviolet light is a form of electromagnetic radiation called actinic or nonionizing radiation. The energy associated with this ultraviolet curing is not sufficient to penetrate into the body and interact with the tissue to produce any dramatic effects such as cancer, which is often associated with "radiation." However, exposure to ultraviolet (and visible and infrared) radiation can cause effects on both the skin and eyes.

Ultraviolet energy, which is less than 1 percent of the sun's incident energy, is intentionally generated by industrial sources. It is often divided into four wavelength ranges, defined as follows:

Description	Wavelength
UV-A:	315–400 nanometers
UV-B:	280–315 nanometers
UV-C:	200–280 nanometers
Vacuum UV:	100–200 nanometers

UV-A, which is the largest part of ultraviolet energy, is transmitted by normal window glass and can increase pigmentation, among other effects. It also is the upper end of the UV range and the lower limit of sensitivity for the human eye.

UV-B radiation is primarily erythrogenic, that is, it will produce marked reddening and other effects, including increasing the pigmentation of the skin. It is also responsible for many of the effects on the eyes.

Natural UV-C radiation is filtered by ozone in the atmosphere, but man made UV-C has important sterilizing properties as well as other industrial uses.

The lamps most often used in the UV curing process include both low and medium pressure mercury lamps. Low pressure lamps, which are not widely used, have typical intensities of one watt per linear centimeter and possess most of their energy around the 254 nanometer wavelength, or in the UV-C range. The use of these low pressure lamps almost always requires the use of an inert atmosphere. The 254 nanometer band, being a relatively shorter wavelength, can be effective in promoting surface cure.

The more widely used medium pressure mercury lamps generally have energy levels of 300 watts or more per linear inch and produce a spectrum of energy at 365 nanometers, but the 313 nanometer band is also strong. These lamps produce a more diffuse light source and provide the energy needed to achieve through cure. In addition to the UV wavelengths, visible and infrared components are also present.

Energy sources, including ultraviolet, infrared and visible, can produce a variety of biological effects. The ultimate effects of these photochemical injuries are determined by both dose rate and length of exposure. This is one way in which photochemical injuries are distinguished from thermal injuries. Biological damage is most prevalent at exposures to wavelengths below 325 nanometers.

The most common effect of UV exposure, whether it be from the sun or from a mechanical source, is erythema, which has been documented since the 1920s. It depends upon the wavelength, exposure time and pigmentation of the skin. Exposures to intense sources of UV radiation can result in dry, brown and wrinkled skin. These effects are caused primarily by UV-B and UV-C exposure, that part of the spectrum in the range of 200–315 nanometers. The longer the wavelength of incident energy, the more severe and persistent the effects are, as a result of the deeper penetration into the upper layers of the skin.

This erythema, or reddening response, usually begins three to four hours after the exposure and reaches a maximum about 12 hours post-exposure. It will generally start to decrease in about 2 to 7 days. Increases in pigmentation generally progress within 15 days to three weeks following the erythematic response and, this reaction could be cumulative in nature.

Effects on the eyes are also primarily due to absorption of UV-B and UV-C bands. These wavelengths are strongly absorbed by the cornea and the conjunctiva. These effects caused by this absorption are generally considered the primary response of the eye to UV exposure and have been called by various terms, including kerato-conjuctivitis, photo-opthalmia, photo-keratitis, welder's flash, arc eye and others. The maximum sensitivity of the eye for the effects described by this condition is to the wavelength of 270 nanometers, while cataracts have been documented from exposures in the 295–320 nanometer band. Exposure to longer wavelength UV-A may also contribute to the formation of cataracts.

Effects on the eye usually occur 6 to 12 hours after exposure but have been seen as early as 2 hours and as late as 24 hours after the exposure. The time at which symptoms occur is inversely proportional to the severity of the exposure. In photo-keratitis, the front part of the eye, the eyelids and the surrounding skin will become very reddened, the individual becomes photophobic, and tearing is common. Other symptoms associated with these exposures include inflammation, pain, burning cornea, and occasionally, a temporary blindness. These overexposures often cause a sensation of a foreign object or sand in the eyes. These acute symptoms generally appear within 2 to 24 hours, usually disappear within 48 hours and are rarely permanent.

Given the effects on the skin and the eyes that occur upon exposure to UV energy , it is necessary to establish allowable exposure limits. The most complete limits have been established by the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute for Occupational Safety and Health (NIOSH). The ACGIH, which is the body responsible for the threshold limit values, or TLVs®, has developed guidelines for exposure to the 200–400 nanometer band. These guidelines are applicable to UV radiation from arcs, gas and vapor discharges, fluorescent and incandescent sources, and solar radiation. They do not apply to photosensitive individuals or those also exposed to photosensitizing chemicals. NIOSH has adopted a similar concept in its criteria document for exposure to ultraviolet light.

In the near UV region, 315–400 nanometers, an exposure limit of one milliwatt per centimeter squared for exposure times greater than 16 minutes has been established. For the actinic portion of the spectrum, 200–315 nanometers, the biological effectiveness curve relating the effects of wavelengths in this spectral region must be considered in establishing the limits. From this consideration, permissible ultraviolet exposures for varying time periods have been calculated and are, for the same exposure time, much less than those for the near UV. The 8-hour exposure limit of 0.1 microwatt per centimeter squared is, in keeping with the general philosophy of the TLVs, the maximum allowable exposure which should prevent skin and eye effects in nearly all workers.

Another potential hazard related to the ultraviolet curing process is the potential exposure to ozone. Ozone is generated when very short UV wavelengths (184 nanometers) are absorbed by oxygen and its formation is greatest during start-up of the lamps. Since most UV installations use air as the curing atmosphere, ozone generation is a rather common occurrence; however, well engineered UV curing equipment will provide sufficient exhaust to maintain a slight negative pressure within the equipment, and thus prevent escape of ozone or other volatile materials into the work area.

If ozone should escape, it can be easily detected, since it has a very strong odor which is easily detectable, even at very low levels, at or below its acceptable workplace limit of 0.1 ppm. This colorless gas will cause biological effects including headaches and fatigue, dryness of the upper respiratory tract, pulmonary irritation, and may also contribute to respiratory infections.

PHYSICAL AND PROCESS HAZARDS OF EB

Electron beam curing is a process where high velocity electrons are absorbed by properly formulated inks, coatings, or adhesives, resulting in the production of free radicals. These radicals are generated throughout the formulation and initiate a rapid polymerization or curing process. The curing extends below the coating surface and thereby overcomes a disadvantage of UV. The amount of heat generated in the EB process is small in comparison to that created by UV curing. Some advantages of EB processes are high production speeds, solvent-free coatings and the ability to cure on heat sensitive substrates.

Most EB systems contain a power supply, vacuum system, source of electrons, material transport system, coating equipment and control console. Thermally emitted electrons are accelerated by a large voltage potential into the curing area. The electrons lose their energy in the formulated material that is being moved through the curing chamber by the material transport system. The amount of electron energy lost is directly related to the quality of cure. If there is no energy loss in the ink, coating or adhesive, the curing process does not occur.

While the loss of electron energy results in curing, it should be noted that some of this lost energy can produce X-rays. This means that EB workers could potentially receive ionizing radiation exposure from both the electrons and X-rays. Since electrons are charged particles that give up most of their energy in a short distance, workers can be protected by electrical capture in unique designs of the equipment. As long as workers are not directly exposed to a flux of electrons, this particular hazard can be minimized. Protection from X-ray exposure is achieved by lining the unit with a material with a low atomic number followed by a material with a high atomic number, such as lead. This combination limits the release of X-rays.

Most of the current knowledge on the biological effects has been developed from short-term, high level exposure incidents rather than from the potential long-term, low level exposure situation which involve EB personnel. The possibility of long-term effects on the large number of workers receiving low, chronic exposures is cause for greater concern than the short-term effects from acute exposures which involved only a few individuals.

When a worker is exposed to ionizing radiation, one or more of four events can happen:

1. The radiation can damage cells, but the damage is repaired.
2. It passes through the cells without doing damage.
3. It damages the cells beyond repair and cells are reproduced in the damaged form for the remainder of life.
4. It kills the cells.

It is obvious that the latter two are of importance since, if enough cells are killed, then the organ can no longer function; incorrectly repaired cells may, over the years, produce adverse effects. Such effects as cancer, shortened life, genetic alterations, cataracts, sterility and erythema have been attributed to ionizing radiation exposure.

It is reasonable to assume that ionizing radiation safety philosophy follows the zero exposure concept, i.e., where there is no dose there is no risk. Such a concept is difficult to achieve but is considered by many to be the most ideal to assure minimal potential injuries. In the practical sense, the goal of "as low as reasonably attainable" (ALARA) is used as the approach.

The current federal guidelines for occupational exposure to ionizing radiation in the United States are found in the Code of Federal Regulations, part 1910.96. The following is an overview of the exposure levels permitted by the Code. Except as discussed below, no employer shall possess, use or transfer sources of ionizing radiation in such a manner as to cause any individual in a restricted area, such as EB personnel, to achieve in any period of one calendar quarter a dose-equivalent (rem) in excess of the following limits:

	Rems per Quarter
Whole body, head and trunk, active blood-forming organs, or gonad	1.25
Hands and forearms, feet and ankles	18.75
Skin of whole body	7.5

An individual can receive a dose equivalent greater to the whole body greater than those given above as long as:

- During any calendar quarter the dose-equivalent to the whole body does not exceed 3 rems, and
- The dose-equivalent to the whole body when added to the accumulated occupational dose-equivalent to the whole body shall not exceed 5 (N-18) rem where N equals the individual's age in years, and
- The employer maintains past and current records which show that the addition of such dose-equivalent will not cause the individual to exceed the amount authorized in the proceeding. Dose-equivalent to the whole body shall be deemed to include any dose of the whole body, gonad, active blood forming organs, head and trunk, or lens of the eyes.

Additional information on existing federal, state and local requirements such as licensing of units and monitoring assessments must also be considered. Most states require the manufacturer or the installer of EB equipment to notify their radiological health agency upon installation. Upon notification, the state will send the user a copy of the applicable regulations and the registration forms which are to be completed and returned.

OTHER PHYSICAL AND PROCESS CONSIDERATIONS

UV/EB curable products can polymerize upon exposure to light, heat and oxidizing agents. Therefore, precautions should be taken to avoid these conditions. Preventive measures to prevent premature polymerization include:

1. Store these materials away from direct sunlight and sources of actinic radiation, such as mercury and fluorescent vapor lights.
2. Keep these UV/EB curable products stored at temperatures ranging between 60 and 80°F. Higher temperature storage can deplete inhibitors used to stabilize the product. Lower temperatures can initiate product phase separation, causing precipitation of the stabilizing inhibitors. This can cause a reduction of product performance properties and stability problems. If phase separation should occur, gently warm and mix the contents of the container to evenly distribute the inhibitor throughout the product.
3. Care should be taken to prevent contamination of the UV/EB products during storage with peroxide, iron particles and other free radical sources which can initiate the polymerization.

For the best cure response, UV/EB curable products should be used within 4–6 months of receipt. Inventory control of the product is important, and it is suggested that the product should be used on a first in, first out basis. Inhibitors have been added to UV/EB products to stabilize and enhance the shelf life of the product. Inhibitors require the presence of oxygen. Thus to prevent "dark cure," headspace needs to be left in the drum storage containers.

Equipment and tools can be cleaned with the prudent use of organic solvents followed by soapy water washes and water rinses. Protective clothing requirements and precautions as specified on the MSDS from the solvent manufacturer should be adhered to. Typical solvents used are methyl ethyl ketone (excellent), isopropanol, methanol, toluene, xylene, acetone and *n*-butyl acetate.

Residual UV/EB curable materials in drum containers can be neutralized with alkaline soapy water wash treatments and rinsed with water. Protective clothing, goggles and gloves should be used. All waste washes and rinses should be disposed of properly in accordance with U.S. Federal RCRA, Canadian Provincial, state and local requirements.

ENGINEERING AND ADMINISTRATIVE CONTROLS

- UV/EB equipment should be installed with manufacturer supervision.
- Operators should be trained by the manufacturer so as to fully understand operating and safety procedures.
- Detailed equipment manuals should be available, providing the operator with safe use and handling information.
- Never look directly into radiation lamp equipment or its reflections from metal surfaces.
- The shielding available at UV curing chambers should be analyzed for its effectiveness and any deficiencies noted should be remedied. The importance of leaving the shielding in place should be stressed to employees.
- For flat line applications, canopy hoods are often used at application points and can be made most effective if they are positioned very close to the line. Side curtains are also useful in reducing the effects of cross-drafts. These canopy hoods serve to minimize acrylate odor and to remove any mist generated during application.
- For three-dimensional UV systems, well-designed and maintained spray booths are an absolute necessity. These units can be bought from many major manufacturers as turnkey systems, which provide for makeup air, capture of the overspray and subsequent exhaust. This type of system will aid in housekeeping and in the reduction of employee exposure.
- All UV/EB curable materials should be pumped from drums rather than manually transferred. It is advisable to avoid high shear pumps (gear, piston) as these may generate excessive heat and cause the coating to react in the pump. Centrifugal, peristaltic, diaphragm or low shear progressive cavity pumps are usually preferred.
- A thorough cleaning of all contaminated equipment should be accomplished by washing with a 10–15 percent solution of hot caustic (sodium hydroxide). This solution is corrosive and must be handled with care and properly disposed of.
- Sideboards should be installed at all material reservoirs to help direct recirculation and control accidental contamination.
- Smoking and eating on the line must be prohibited as these activities may contribute to accidential employee exposures.
- An eyewash/safety shower should be available in the immediate vicinity of the line.

Additionally, in EB Processing:

- All employees should be trained in the general aspects of safe operation of electron beam equipment.
- The importance of operating the EB processor as designed to control potential hazards, along with ozone and oxide of nitrogen which are generated, must be stressed.

- Employees should be monitored for exposure to ionizing radiation with film badges.

PERSONAL PROTECTIVE EQUIPMENT

While it is most desirable to use engineering and administrative controls to limit employee exposure, there are times when the use of personal protective equipment is absolutely necessary. Wearing eye protection in the form of safety glasses with side shields or chemical splash goggles should be mandatory during chemical handling. If additional protection against UV sources is desired, glasses that meet the National Institute for Occupational Safety and Health (NIOSH) recommendations for protection against UV light are available. Additionally, the wearing of contact lenses by anyone handling chemicals should be strictly prohibited.

For skin protection, polyethylene is the recommended construction material. Gloves, boots, forearm length sleeve guards and full body suits are available. Items made of nitrile rubber are also acceptable. For casual contact, suits made of synthetic materials such as Tyvek® are very inexpensive, disposable and effective. Supplements which can be used are barrier creams. These should never be viewed as a substitute for proper handling procedures and the judicious use of personal protective equipment.

Some type of safety shoes should also be worn by employees working with UV/EB materials. Shoes and other items made of leather which become contaminated with the UV/EB materials must be discarded. Other clothing and uniforms which become contaminated can be professionally laundered and reused.

For the new three-dimensional spray technologies, respiratory protection may be necessary. While the use of a properly functioning spray booth is mandatory, supplemental protection in the form of NIOSH/MSHA-approved air purifying (TC-23C) or air supplied respirators (TC-19C) may be required. Each situation should be evaluated individually before it is assumed that respiratory protection is required. This can be done by evaluating airborne concentrations of paint overspray, reactive diluents and solvents, along with an assessment of the booth's effectiveness in removing these materials.

SPILL AND WASTE DISPOSAL

If a major spill should occur, use the following procedures:

- Wear protective clothing and NIOSH/MSHA approved respiratory equipment as discussed above.
- Isolate and dike the area of the spill.
- Cover the spill with saw dust, clays, activated charcoal or other absorbing material.
- Saturated absorbing materials should be disposed of in accordance with waste disposal regulations in your area. Contact with these waste materials should be avoided.
- Wash area thoroughly with alkaline soap and water.
- Wash and rinse waste water should be disposed of again in accordance with Federal RCRA, state and local government regulations.

SUMMARY

This chapter has reviewed several important occupational health concepts and how they apply to the safe handling of UV/EB curable materials. The primary concerns with these materials are their potential effects on the skin and the potential process hazards involved. Careful planning of a radiation cure installation and employee education and training will minimize the potential for these adverse effects to occur.

Chapter Six

INDUSTRIAL PROCESSES

INTRODUCTION

The use of ultraviolet and electron beam processing has grown steadily since the late 1960s. A summary of the product market areas that use curable inks, coatings and adhesives has been given in Chapter 2. Commercialization of these products has occurred to a large part because of advantages in the plant such as reduced space, lower energy requirements and increased production speeds. Application of this technology to a given product can be a moving target which is influenced by cost, price, performance, new materials, improved raw materials, government regulations, competitive considerations and advances in equipment performance. This chapter will help put it all together to produce a commercial product.

THE DECISION PROCESS

The decision to use UV/EB processing for a particular product requires the evaluation of a number of factors, both technical and financial. The decision involves the following:

TABLE 1: FACTORS IN SELECTION OF A SYSTEM

Product to be manufactured
Curing equipment — new or existing?
Application equipment — as is, retrofit, new?
Product performance — equivalent or improve?
Substrate
Cure — UV or EB
Curing equipment cost
Cure speed required
Curing power
Coating application
Coating thickness
Coating method
Coating viscosity
Coating performance requirements
Surface finish
Coating use volume
Coating color
Coating cost
Technical support

Plant technical ability
Quality control
Personnel requirements
Safety
Product loss
Waste disposal procedures and cost
Electrical service
Electrical rates
Electrical supply
Storage facility
Equipment maintenance
Conversion cost
Down time for conversion/start-up

These 32 factors cover most but not necessarily all of the considerations used in selecting a UV or EB curing system. The factors of product to be made and the equipment to be used determine the available options. The greatest number of options are available if a new product is to be made on new equipment. The options are limited if an existing product is to be made on existing equipment.

As an example, consider if a UV/EB curable product is to replace a current product using existing equipment. The existing product's performance would have to be matched or improved. Frequently, if the conversion is successful other products manufactured by a company will be converted to this technology.

To cite an example, if the current product is a flat continuous 20-mil gauge surface treated plastic web, 60 inches wide, with a single coating, 1 mil thick, applied by a roll coater from a 30 percent solids solution. The coating is dried by a heated forced air oven. The product is produced to order for three customers in lots of 20,000 to 150,000 feet. The coated film is available in three colors. The existing coated product has good film adhesion, good mar resistance, passes a 1/4-inch mandrel bend test, a 500-hour light stability test, and meets a color match standard for each color.

To accomplish the goal of changing the existing product from a thermal system to a radiation cured system, a development program is required to select the coating, select the cure process and equipment, and test the final product. This can be done internally if a pilot line is available or alternatively custom coaters have toll facilities for both EB and UV product development programs. Since the goal is to use the existing plant equipment, the production line must be analyzed to determine if the space is available to install the curing equipment. For EB, an oven can be removed or shortened, but then other products may not be able to be manufactured on the line. Ultraviolet units can be installed in a smaller space, or even within existing ovens. After doing a cost analysis, it is determined for this application that the capital investment for EB is too high, so UV is the choice. For UV cure equipment the options are electrode or electrodeless lamps coupled with the decision for doped or undoped lamps and medium pressure versus high pressure lamps. The differences between these options were discussed in Chapter 3, Ultraviolet and Electron Beam Curing Equipment.

The line is equipped with a roll coating head. In ultraviolet and electron beam curing, 100 percent of the material applied is present after cure. Thus, frequently there will be the need to change application methods. In this example, gravure application would be required. The line will therefore need a set of gravure rollers, an oscillating knife head, variable speed controls on the coating head and line, jogging capability, an interlock system, ramping ability a constant line speed ability, and tension control between the let down drive and the take up drive.

Elastomeric (rubber) rolls that come in contact with the uncured coating must be replaced with special rolls which do not swell or interact with the UV/EB curable materials. Most roll manufacturers make rolls for UV/EB cure systems. The interlock system should be such that the UV lamps cannot be turned on unless the line is running. If a recirculating system is used on the coating head, it should be a low shear system such as a diaphragm pump and designed to minimize air bubble incorporation into the coating.

Evaluation of available coatings needs to include the initial quality control tests of color match or value, viscosity at a predetermined temperature, an infrared spectrum, a gel permeation chromatograph (GPC), oven stability test and a cure rate test. By starting these tests during the development program, a history is developed which is useful for predicting lot to lot variations as commercialization proceeds. Differences in results can be due to variations in lots as well as changes in experimental design. For the development and commercialization phases, samples should be taken from unopened containers, containers should be dated upon receipt and materials should be used prior to the expiration date. Discard materials after the expiration date of the manufacturer following the recommended procedure.

Preliminary screening of the coating can be done with laboratory drawdowns on cut sheets using drawdown bars or Meyer rods (wire wound rods), affixing the sheets to the web, and running under the lamps at the proper speed. This can be used to test alternate film pretreatments, formulation modifications and a general comparison between several coating systems; however, the only way to get a true evaluation of the system is to make an actual run of several thousand feet. Some production difficulties only become apparent in a long run. If a comparison of several film substrates is required, a composite roll of film should be made of 50- to 100-foot lengths spliced together in a repeating pattern after a leader length. The composite samples should be placed at the beginning, at one-third, two-thirds, and at the end of the run. During the run the viscosity of the coating solution should be monitored and recorded. Changes in viscosity can produce changes in the applied coating to the web. Unlike solvent or water-based systems, "what you see or put down is what you get" in your product. The art in applying UV/EB curable materials is gained by experience with the operating system.

The pilot (or production) line start up is as follows:
1. Start web with ramp up procedure
2. Start lamps
3. Start coating when the lamps reach full power
4. Adjust line speed
5. Adjust coating head
6. Adjust or set smoothing operation, if required.

To take a sample, lift the coating head to stop the coating application and shut the line down after the last uncured material has been cured by the lamps. The line can be restarted to line speed, starting the lamps, and lowering the coating head to resume coating. The first set of experiments with each coating head configuration should be a line speed, viscosity study. The coating thickness, or coating per unit area, and surface appearance is a factor of line speed, coating viscosity and coating head. It is important to remember that when an existing product is being matched, the viscosity of the UV/EB curable coating will be greater than that of a solvent or water-based coating. The use of a temperature controlled coating head and circulating system at an elevated temperature of 35–45° C gives improved control, but may reduce the stability of the coating. If the coating specifications are tight, this can become a requirement rather than an option. For example, if a solvent based coating has a dry thickness requirement of 1 +/– 0.05 mil thickness using a 30 percent solids solution, the applied coating thickness would be 3.3 +/– 0.16 mils. The UV/EB curable coating, however, would be applied at the 1 +/– 0.05 mil, since it is a 100 percent solids system. The solvent coating could be applied by a roll coating method such as knife over roll, while the 100 percent solids coating would require the gravure roll. UV/EB cured products are presently produced under these or even tighter specifications. When converting an existing product, as in this example, the coating head may have to be rebuilt or replaced to maintain the tight tolerance. The introduction of microprocessor controlled coating heads has simplified coating under narrow tolerances.

In the conversion process, the performance of the product cannot be altered. For this example, the performance requirements are color matches, mandrel bend, film adhesion and light stability. This conversion should not impact the mar resistance or mandrel bend. The colorants used in the original product may not be suitable for use with UV, since some dyes and pigments are incompatible and some experience a color shift when exposed to UV. To adjust for this fact, color matches are checked by curing the material under production conditions and then checking the color. This difficulty does not exist with EB curing. Light stability of a colored UV product can be affected by the photoinitiator system used, since some initiators increase the yellowness of the product. In addition, some UV stabilizers used in conventional systems can interfere with the UV cure. If a UV stabilizer is required to maintain the light stability, several companies offer stabilizers which are designed to give a window for UV cure and also recommend the photoinitiator to be used to maximize the use of the window. In electron beam cure the stabilizer used in the original product should be satisfactory.

DEVELOPMENT OF A FORMULATION

Whether a company formulates itself or has a formulator supply the material, the question which must be answered is: Which needs to be addressed first, the desired properties or the viscosity? The product's properties are determined by the formulation, but the resins (oligomers) in the formulation used to achieve the properties impact the viscosity. In addition, the method by which the coating is to be applied requires a specific viscosity range. Unlike solvent based coatings, the materials used to reduce the viscosity of the oligomers are reactive diluents, that is, they become part of the final film formed, and changes in the amounts of these diluents will change the final film properties. Thus the balance between properties and viscosity must be kept in mind during the development of the formulation.

What does the compounder have to use? (The chemistry has been reviewed in Chapter 4.) Table II summarizes the materials used in a formulation and the general effect each has on the final properties. Parts per hundred parts resin (PHR) rather than percentage basis is frequently used in the manufacturing environment. Whatever the basis of the formulation, be sure everyone uses the same system. The difference between PHR and percentage formulations can seem small but can give large changes in the final product properties.

TABLE II: FORMULATING INGREDIENTS

Ingredient	*Characteristic*	*Amount Used (PHR)*	*Results In*
Oligomers	Hard resins, such as epoxy acrylates	0–100	Stiff, hard, low extension
	Soft resins, such as urethane acrylates	0–100	Flexible, soft, high extension
	Blends of hard/soft oligomers	5/95–95/5	Intermediate
	All low molecular weight	0–100	Stiff, brittle, low extension
	All high molecular weight	0–100	Flexible, more extension
	Monofunctional	0–3	Softer
	Difunctional	100–90	Most are difunctional
	Multifunctional	0–10	Hard, stiff, low extension
Monomers	Single double bond	0–80	Lower viscosity
	Multiple double bonds	0–45	Increase bondscrosslink density, stiff, tough
	Mixed functionality (unsat. plus acidic basic, etc.)	0–10	Adhesion, modify properties
Other resins	Nonreactive (VYGH for ex.)	0–15	Plasticize Reduce cost
	Reactive type (polymeric amines)	0–15	Adhesion Modify properties
Photoinitiator	Free radical	0.25–5	Cure speed, shelf life
	Cationic type	2–5	As above
Photosensitizer		0–5	As above
Chain transfer		0–0.5	Controls molecular weight
Stabilizer	For raw materials	20–200 PPM	Shelf life
	For formulation	As required	Inhibits pre-cure
	Light stabilizer	As required	Color change, properties
	Heat, hydrolytic, etc.	As required	Prevent property loss
	Antioxidants	As required	Inhibit oxidation
Surfactants	Dispersants	0–1 PHR	Disperse pigments and fillers
	Flow Modifiers	0–5	Flow out leveling
	Emulsifiers	0–1	Disperse oligomers in water, monomers
	Defoamers	0–1.5	Reduce foam, air bubbles
	Other	0–1	Wetting, prevent phase separation
Pigments, Fillers,	Flatting agents	0–45	Viscosity, color, cost, cure
Dyes		0–5	Color, cure
Adhesion Promoter		0–5	Adhesion
Coupling agents		0–0.5	Adhesion, aid in pigment binding
Viscosity stab.		0–1	Viscosity
Dual cure additive		0–3	Shelf life, second cure needed

In addition to the possible ingredients listed in Table II for 100 percent solids systems, formulations are commercially available which have been reduced with either solvent or water. These options are used to reduce viscosity when the addition of the monomers will alter the required physical properties. For recommendations on specific raw materials contact the suppliers of the materials. RadTech International maintains a list of suppliers to the industry.

Before using an additive that has not been previously used in a UV/EB curable formulation, it is best to test the additive in a standard formulation. For this purpose, a standard formulation is one which has been characterized for its critical properties. Materials such as pigments and fillers may be surface modified to improve dispersability. This modification may interfere with the initiator systems. Some fillers may initiate monomer polymerization causing gel or filler agglomeration.

In compounding, high shear conditions are to be avoided at high viscosities to prevent polymerization. The viscosity of a freshly mixed formulation should be taken immediately on a bubble-free sample and again at 24 hours. Often the viscosity will change during this period. One cause for this change is moisture absorption which occurs during processing. Some monomers and oligomers, such as hydroxy-containing acrylic monomers, polyether-based urethane acrylates and acrylated polyethers, are hygroscopic. Hygroscopic materials absorb moisture. This moisture causes a steep change in the viscosity of a dry oligomer system. Another source of moisture can be high surface area pigments or fillers. Some oligomer manufacturers stabilize their oligomer viscosity by the addition of small amounts of water (0.1–0.5 percent) or low molecular weight alcohols or amines. The low level addition moves the system out of the steep portion of the viscosity curve. Moisture pick up can also affect the cure speed in UV cured products.

As in any formulating operation, the order of addition, the use of master batches and letdown procedures all impact the quality of the product. For UV curable formulations, the photoinitiator is the last ingredient added. A formulation developed for electron beam can be converted to UV curable by the addition of the initiator system, but the properties of the cured formulation will usually be slightly different. These differences are due to changes in the start of the chemical reaction (polymerization) and the resulting structure of the polymer network. UV curable formulations can be cured by electron beam, with or without the presence of the initiator. Again the properties will be slightly altered.

UV/EB curable formulations that are tack free, or "dry" are made for use as photoresists or adhesives. The formulation is transferred with heat and pressure to the substrate prior to UV/EB curing.

Many formulations are filtered either before use or as part of the recirculation system used at the coating head. Filtration is used to remove any gel, pigment or filler agglomerates before they can cause problems in product performance. The simplest filtration is to use lint-free cheesecloth or a fine mesh screen. For critical applications in electronics, magnetic media and microfinishing products, pressure filtration through a cartridge may be required. Compounding of this type of critical product is done in a cleanroom.

Finally, the formulator should remember that the majority of the oligomers and monomers shrink as they react. The cured coating is smaller in volume than the uncured coating. A few monomers are available which expand as they react but their current cost and availability limits their use. Shrinkage can lead to residual stresses that can cause product distortion or loss of adhesion. The stress increases with the thickness of the coating and is most pronounced over large flat surfaces.

APPLICATION METHODS AND SURFACE PREPARATION

Each method of application has a working viscosity range that will produce an acceptable coating appearance. In addition to the viscosity, the thixotropic properties of the formulation will determine the coating's appearance. The thixotropic properties are a measure of the "leveling" or the resistance to flow of the applied coating. Table III shows the variation in viscosity for various printing methods.

TABLE III: PRINTING INK VISCOSITY RANGES

Printing Method	*Viscosity at 25° C*
Gravure	30 – 200 cps
Flexographic	50 – 500 cps
News ink	200 – 1,000 cps
Screen printing	1,000 – 50,000 cps
Letterpress	1,000 – 50,000 cps
Lithographic	10,000 – 80,000 cps

Thus a UV ink developed for a screen printing application could not be used without reformulation in a gravure printing application.

UV/EB curable formulations have been commercially applied by every coating method, except possibly brush coating. Air-knife coaters, rigid knife coaters (both supported and unsupported), metering rod (Mayer rod) and puddle (flexible blade) coaters are used but suffer from the "what you see is what you get" principle, since the coatings are cured so rapidly after application. Curtain-coating and flow coating applications require low viscosity formulations and are generally limited to clear or low level filler compositions. Curtain coating is used by the wood and flooring industries for flat stock. Flow-coating is used for three-dimensional products such as automotive wheels, hubcaps, golf balls, etc. Some short-run three-dimensional products have been coated using dip coating, but generally spray coating is preferred. Airless and air atomized spraying are used with the proper safety precautions for the overspray. These methods suffer from the loss of larger amounts of coating in the application due to overspray. Electrostatic spraying formulations are available and greatly reduce both the potential employee exposure and the product loss in the spraying application.

Roll coaters of every type have proven useful with UV/EB curable formulations. Generally, as the product line of UV/EB curable products develops and expands, the roll coating heads used become more advanced. Kiss-roll, transfer-roll, direct gravure, offset gravure, vertical reverse-roll, three-roll nip feed and customized variations of these coaters are all in use on the commercial scale. No matter which form of roller coater is used, there are limits on the viscosity of the composition. Each class of roll coating heads has an optimum viscosity range and some coating head configurations are more sensitive than others.

Transfer coating of dry photoresists and adhesives is used in products where a tack-free product is required prior to ultraviolet or electron beam curing. Transfer printing of UV cured inks in decorative containers, and other specialty printing needs has been commercial since the seventies.

Textiles are coated by calendaring or direct coating. For sizing and filling operations the best cure is obtained with electron beam. Topcoats are applied by roll coating and can be light or electron beam cured.

If the coating is applied in a continuous web, the web tension is more critical for any application method than the corresponding solvent or water-based system.

Small changes in web tension usually result in corresponding changes in the coating thickness. The web tension should be included in any computer monitored or controlled operation.

The coating thickness that can be applied is determined by the type of process used, the curing process, the available curing energy, the line speed (or rate of exposure), the surface effect desired, the level of pigments or fillers used and the reactivity of the formulation.

Screen printing or serigraphy, in which the coating is forced through a screen or stencil, is used when a precise thickness is required. Using a 100 percent solids system a coating of 250 microns (10.0 mils) down to about 3.8 microns (0.15 mils) can be applied with a good degree of tolerance. Screen printing of UV/EB curable coatings is used in applications as diverse as printed circuit boards, membrane switches, backlit display panels, four color posters and irregularly shaped cosmetic containers. Generally screen printing becomes slower as the screen size decreases. The advantage of these coatings in screen printing is that they do not dry on the screen. The disadvantage is that these coatings can have gel particles which can clog the screen. Properly filtered coatings do not present a problem. Higher production rates can be achieved by switching to precision or gravure roller coating methods. This higher production rate is at the loss of some degree of tolerance, difficulty in applying coatings under 12.5 microns (0.5 mils), difficulty in uniformly coating wide webs at the heavy end (250 microns) and the requirement of a flat surface.

Curtain coating gives a minimum coating thickness of about 50 microns (2 mils) and is used more on sheet type products such as particle board, wall panels and flooring. To achieve the minimum coating thickness it is usually necessary to heat the coating to reduce its viscosity and run the line speed at up to 185 m/min (600 fpm).

The application of colors in printing or coating is dependent on the absorption characteristics of the pigments. Blacks, whites and blues absorb short wavelengths in the UV range. Because this absorptivity slows the cure rate, these colors are generally applied first in UV cure. If an electron beam is the curing equipment, the rheological considerations used in thermal printing can be applied. If a UV cure is used, either as an interstation cure or as the final cure, the preferred order of application is: (1) Black or white applied first even when the coverage is heavy. (2) Blues applied second down unless very light coverage is being used. (3) Reds including magenta down third. (4) Yellows down fourth. (5) Overprint varnish down last. White is most often used in metal coating in contrast to black which is most often used for paper or foil applications. One exception to the above order is in the printing of wood grains. For this application the background color is usually brown and it is applied first followed by the blacks, dark browns and oranges. This is possible since the blacks are usually applied lightly in this application.

Clear radiation cure coatings are noted for their high levels of gloss and their retention of gloss. Even pigmented coatings usually have a higher gloss level than the corresponding solvent systems; however, sometimes it is desired to have a flat or matte appearance for applications in the graphic arts, wood finishing, instrument panels, packaging, laminate finishes and appliance industries. The high levels of flattening pigments commonly used in solvent systems are not effective in UV/EB curable systems; however, two curing techniques have proven successful in gloss reduction.

The first method is effective with both UV and EB curable coatings. The uncured wet film containing the flattening pigments is first given a partial UV cure in air or an EB cure of 1–3 MR in a variable oxygen (air) atmosphere. In the UV method the photoinitiator should be one that is inhibited by oxygen. Both the UV and EB methods are finished by a second cure step in an inert atmosphere, usually nitrogen. This process can be used to produce 60° gloss values between 10 and 90 percent. In this method the body of the coating is curing first and forcing the flatting agents to the uncured surface, which is then cured in the second stage cure.

The alternative method for gloss reduction provides a textured surface to reduce gloss, but it is difficult to control for intermediate gloss levels. The formulation does not require flatting agents. The coating is cured under low power germicidal lamps (8-15 watts per inch) in an inert atmosphere to give a partial cure. The cure is completed by using a standard UV air or inert cure. Alternatively, the cure can also be completed by using EB. In this method the surface is micro-crinkled in the first stage and the bulk of the coating is cured in the second stage cure. Both of these methods for gloss reduction require two curing stations.

Unlike solvent or water-based coatings there is little attack by a ultraviolet or electron beam curable composition on the substrate to cause swelling or other surface changes, and there is little if any heat in the rapid cure. Therefore, other methods of obtaining adhesion must be used. Thermal bumps after curing are used in some installations. In film-based products, film manufacturers have developed surface treatments to make the films receptive to UV/EB curable compositions. Some formulations contain reactive monomers which promote adhesion to a given substrate. Adhesion promoters are also available. Some manufacturers have made use of the shrinkage of the coatings on curing by slightly roughening the surface of the substrate. The cure shrinkage then gives some mechanical adhesion to supplement any chemical bonding. Curing a coating on a round substrate gives a compressive force at the interface, which increases the adhesion.

The use of 100 percent solids systems increases the need for a clean substrate surface. A clean surface is not only free of dust, lint and oil but should be free of any processing aids such as mold release agents, surface applied antistats and other additives that may bloom to the surface. If it is not possible to remove the surface processing aid, it is usually possible to formulate to compensate for its effect.

Surface treatment to improve adhesion includes corona discharge, high intensity ultraviolet irradiation (with and without a photosensitizer), chemical or solvent etching, attaching chemical reactive groups and proprietary treatments used by film manufacturers.

RETROFITTING EXISTING EQUIPMENT

When existing coating equipment is to be used with UV/EB curable materials, some changes are required. Rubber or other elastomeric rolls that will come in contact with the uncured coating must be replaced with special rollers designed for this use. Most major roll manufacturers have these rolls. Recirculating pumps, hoses and other parts of the recirculating system should be inspected and rubber parts should be replaced with materials suitable for use with these compositions. Any brass, copper or bronze parts that come in contact with the composition may have to replaced. Printing plate manufacturers should be contacted for their recommendation concerning the proper plates to use. The exhaust system at the coating head and at the mixing area needs to be adequate for these materials. The entire coating unit and area should be thoroughly cleaned including the overhead beams, ducts, etc., prior to the conversion.

For any web system, all bearings should be checked for alignment and play. Backup rolls should be checked for roundness (eccentricity), linearity and distortion under pressure. The system should be free of chatter and be able to maintain the set pressure for the web. If a UV cure unit is installed, the unit should be checked after installation for stray or scattered light. Additional shielding may be required to protect personnel and to prevent premature polymerization of the formulation. If air or hydraulic pressure is used to control the coating nip or knife, a higher pressure setting may be required to maintain a uniform coating. As previously mentioned, an interlock of the drive and lamps is required for a UV curing unit to prevent the lamps from burning a stopped web. For electrode lamps this is usually a shutter system and for electrodeless lamps the lights are turned off. An interlock is usually installed on the electron beam systems that shuts down only the beam, leaving the remainder of the system running.

If an existing letterpress system is to be equipped with a UV system, the additional heat generated by the infrared energy from the light may cause press problems, due to the heat absorbed by the press. Most press manufacturers can give recommendations for retrofitting their units to minimize these effects.

Often the curing equipment manufacturer, the materials supplier or a consultant can recommend the correct retrofit for the given process.

SUMMARY

There are many applications for which the UV/EB curing process can be commercially used to benefit both the convertor and product performance. These benefits are best realized when all parties to the process, i.e., the materials supplier, the equipment supplier and the fabricator or convertor, work together to produce the best system for a given installation.

Chapter Seven

TRAINING PERSONNEL FOR A CURING OPERATION

OVERVIEW OF THE TRAINING PROGRAM

Once the decision to install a curing system has been made, a training program should be designed with the help of the curing equipment manufacturer and the material supplier(s). The program must comply with federal, state and local regulations on occupational safety and health, environmental protection, worker's right-to-know, and community right-to-know laws. In addition to complying with the law, it is necessary to provide knowledge and understanding to a new process.

A good training program should protect workers, meet the regulatory requirements, make for an easier transition to the new process, and reduce losses. The program should cover at least the following:

1. Curing system (UV or EB).
2. Substrate — what the chemistry is being put on.
3. Chemistry — the ink, coating or adhesive.
4. Equipment clean up, repair and maintenance.
5. Waste disposal.
6. Personal hygiene and safety controls.
7. Emergency procedures.
8. Identification of available personnel who know about the new process.
9. An emphasis on the similarities and differences between the new and old process.
10. A review of the MSDS and any other safety information with regard to the ink, coating or adhesive.
11. A summary of the above.

To make the plant employees more secure, the training program should be presented by the lowest level adequately trained supervisor who was involved in the development process. For the introduction to plant personnel, it is useful to have any of the technical staff and any plant personnel who worked on the development — the safety manager, the shift foremen, the plant manager, the shop steward and a union officer — present. At the end of the formal training program, it is recommended that supervisory personnel leave so that questions and concerns can be raised that may not otherwise be asked.

IMPLEMENTATION OF THE TRAINING PROGRAM

Obviously this program needs to be modified for each particular installation and it can only be used as a guide. It has been developed for a large installation which has many diverse departments, all of which require training, since this is the most difficult situation to handle.

The first group of people to receive training on the new process and its implications should be the development staff for the project, engineering, safety, quality control and plant management. The medical department must be provided with information on the expected hazards, MSDS for any hazardous materials, etc. They need to obtain the needed information early in the program in order to handle any situations which could occur during the development program. The safety department needs to be provided with safety information on the curing equipment from the engineering department and MSDS for all the process materials by the research development group. When the start-up is imminent and when all the above departments are ready, the senior officers of the union need to be introduced to the new process and be provided the MSDS and other safety information. They need to have a forum to ask questions about the process and the equipment.

The use of the term radiation cure can cause problems with the introduction to the new process since many people confuse the term with nuclear radiation and thus become unduly concerned. Alternate terms are: fast cure, UV cure and EB cure. Care must be used to thoroughly explain that the use of the term radiation involves light or electrons, not nuclear radiation. The use of an alternate descriptive term can help with the understanding, but it can also be viewed as an attempt to conceal potential danger. Proper worker understanding as to the intent of the terminology is thus important. The training process can be further complicated in many companies by the desire to keep confidential the implementation of the new process, since the purpose for the changeover is frequently to achieve an edge over competition.

By tracking the raw materials through the plant to the finished product, it is possible to determine which plant personnel to train and the level of training each requires in order to perform their job safely and efficiently. A check list for possible departments is:

Receiving — anyone who handles the raw materials
Warehouse personnel
Mixing and compounding personnel — anyone who prepares the chemistry for plant use
Incoming inspection department
Plant material transfer personnel
Production
Supervisors
Engineering
Maintenance
Safety
Medical
Quality assurance
Cleaning crew

Waste disposal
Shipping

It becomes readily apparent that many departments must interface and be trained in the new process and its associated materials.

OUTLINE OF TRAINING PROGRAM

Consult RadTech International North America, 60 Revere Dr., Suite 500, Northbrook, IL 60062 U.S.A. (phone 708/480-9576) for resources to assist with the program. Also consult the appropriate sections of this primer.

Section I — Why?

Explain why the company has made the decision to convert to this technology. Frequently there is a combination of benefits such as energy savings, value added to the product, competitive edge, new product which can be produced no other way, regulatory considerations such as VOCs, improved product performance, increased throughput, etc.

Section II — What is this new process?

Explain the new process is the conversion of specially formulated inks, coatings or adhesives from their wet state to a dry film in the matter of tenths of a second by using either ultraviolet light or electrons to start the reaction. The ultraviolet light is the same type of energy that the sun provides and electrons are part of everything in our world. Explanation should also be given at this point as to why the process can be called radiation curing, i.e., because it involves the radiant energy of ultraviolet light and electron beams. Radiant energy is also visible light, microwave and radio waves with which people are familiar.

Section III — How does this process work?

Explain that the ink, coating or adhesive is designed so that when it is exposed to either UV or EB it will immediately become a solid.

Section IV — Other products

It is useful to show plant employees the variety of other industries which are successfully using this technology. Examples are graphic arts, metal decorating, automotive, fiber optics, plastics, appliances, flooring, magnetic media, dental, medical, etc. Consult the chapter on applications for various uses for these products.

Section V — Substrates

This is closely related to the previous section. Again, showing the variety of substrates such as metal, paper, glass and plastics, helps employees realize the wide use of these materials and increases the comfort level with the new process.

Section VI — Basic Formulation

For this section consult the chapter on chemistry. The formulation (ink, coating, adhesive) is a mixture of the following components: Oligomers — analogous to resins of conventional systems; monomers — analogous to solvents, except that they do not evaporate; photoinitiators — if the system is UV; stabilizers; antioxidants; flow additives; pigments; dispersing aids and others.

Section VII — Safety and Handling

Consult the safety chapter for assistance in development of this section. Included in this area should be discussions on safe usage of the curing equipment, the formulation, the substrate transfer system, clean up, waste disposal, personal hygiene, engineering controls which are in place and why, and emergency procedures. This section is unique to each application and needs to be developed at the plant level. Key portions of each of the above are highlighted in the following sections.

Section VIII — Lamp System

Describe the basic principles of the lamps as found in Chapter 3, Ultraviolet and Electron Beam Curing Equipment. The lamps are of high intensity. Provide information on the particular system in the installation, such as wattage, length, etc. Show the employees what the lamp looks like. Explain that looking directly into a lamp when it is on is like a welder's arc or looking directly into the sun. Therefore there is shielding around the lamp and an interlock system which should never be overridden. Also, skin exposure to the direct light can cause "sunburn." As with any electrical equipment there are electrical hazards. The lamps and their housing can become hot, so be careful to avoid thermal burns. Also discuss how to handle, clean, dispose of the lamps, and procedures for broken lamps. If an electrode arc lamp system has been selected, explain how the ozone removal is being handled and the need for warm-up of the lamps prior to use. For an electrodeless lamp system, explain how the potential microwaves are being detected and the built in safety controls for them.

Section IX — Electron Beam

Explain the principles of electron beam operation as found in Chapter 3, Ultraviolet and Electron Beam Curing Equipment. Describe the shielding which has been installed on the unit and the need for the badges.

Provide all safety information recommended by the equipment manufacturer.

Section X — Substrate Hazards

Describe the material handling system which will be used. Be sure to point out any unique hazards such as static for plastics, edge cut potential for webs, etc. Also discuss how to handle uncured product on the substrate in the event the formulation has been applied to the substrate and the curing equipment fails.

Section XI — Formulation

Discuss the fact that these materials can cause an allergic reaction and therefore care should be taken not to get the materials on the skin. Outline the procedures chosen for this plant such as gloves, disposable uniforms, barrier creams, etc. Also present any safety rules concerning the formulation, such as wash-up prior to eating and using the restroom, and the use of safety glasses. All spills should be cleaned up immediately, and the plant needs to be kept clean so that an unprotected person does not accidently come in contact with the ink, coating or adhesive.

Discuss the difference in the hazards associated with the wet material and the cured film. Discuss the ventilation which has been provided, why it is there and the need to have it operational. Emphasize the location of eye-wash stations, safety showers, wash areas, diking materials, etc. Explain that for some people these materials can produce a rash similar to poison ivy, but as with poison ivy, contact is necessary. Stress that people with rashes or other allergic reactions should avoid direct contact with the formulation while their allergy is active. Some work practices, such as testing tack with the finger or keeping a cleanup rag in the hip pocket may need to be changed. A review of the MSDS should be included here.

Section XII — Odor

Since these are different materials than the plant has been using, it is not surprising they will smell differently. Explain they have a unique odor and a low odor threshold, and therefore a small amount of them in the air is detectable.

Section XIII — Clean Up

Discuss the appropriate clean-up procedures for the operation. Consideration needs to be given to protective clothing, gloves, solvents, waste containers, and avoidance of contact with the waste mixture (especially care that it does not run inside the gloves).

Section XIV — Spill Procedures

Discuss the spill procedures to be used. Consider the immediate removal of contaminated clothing and wash up if skin contact occurred, notification of supervisor and/or safety personnel, location of absorbent materials, how the contaminated absorbent material is put in the waste container, labeling of the waste container, washing the spill area and cleaning the machinery.

Section XV — Waste Disposal

The cured product can usually be handled as regular waste. Wipes should be placed in waste drums. Waste drums should be disposed of in accordance with the regulations. Try to keep uncured waste to a minimum.

Section XVI — Personal Hygiene

This section should include the following applicable points:

1. Use the proper protective equipment such as barrier creams, uniforms, gloves, coveralls, safety glasses, disposable booties, etc. For major spills use any additional required equipment, such as respirators, face shields, etc.
2. Wash up upon direct contact, prior to breaks and before using the restroom. Showers should be taken at the end of the shift.
3. Shoes or clothing contaminated with the uncured material should be changed immediately.
4. Personal clothing contaminated with the uncured material should be isolated and washed separately using a strong detergent. Do not wash with other clothes at home! Contaminated shoes must be discarded!
5. Clean up all spills immediately, regardless of size.
6. Keep work area uncontaminated.
7. Dispose of all contaminated containers, rags, gloves, etc. in the proper container.
8. Use common sense. Know the location of emergency equipment such as safety showers, eye washes, wash up stations, diking and clean-up equipment.
9. If formulations are swallowed or get in the eyes, seek medical attention.
10. If a rash develops, seek medical attention and notify appropriate personnel.
11. Remember the formulations only dry when exposed to UV light or electron beams, so that a small amount can go a long way in contamination.

Section XVII — Emergency Procedures

This section is specific to the given facility. Procedures should be consistent with the overall emergency plan for the site.

Section XVIII — Summary

Remind employees this technology has been in industrial use for more than 25 years in a wide range of industries from printing and wood finishing to automotive parts and electronic applications. Adhesives, coatings and inks which are going to be used in this process are in use everyday by workers in other plants. The information presented is to help them do their job safely and efficiently. Emphasize the worker's responsibility in the procedures and the safeguards the company has developed to protect the employee.

The above is provided as a starting point for a plant training program. Each program must be tailored to the specific process which is going to be used. Consult the appropriate chapters in this Primer to supplement the training program as needed.

ADDITIONAL TRAINING FOR A COMPOUNDING OPERATION

The compounding or mixing area for UV/EB curable systems should be separated from the other compounding area in order to prevent cross contamination. The operators must understand the importance of the weighing operations and that adjustments to the formulation are to be made by the quality control department or by instructions from a supervisor. Batch tickets and history cards must be maintained and followed. The appropriate quality control tests and specifications must be established. Consult the *Radiation Curing Test Methods* book published by RadTech International for assistance. The importance of first-in, first-out for both raw materials and finished products must be established.

In order to achieve a uniform product and reduce batch to batch variations, the temperature of each component must be controlled. Frequently, the high viscosity oligomers are heated to aid in material transfer and the monomers are heated to help with mixing the batch. Operators should be trained in the safe handling of the raw materials with special attention given to the monomers which can cause skin irritation and photoinitiators which are activated by light.

The compounding department, the incoming inspection department and the exit quality control department all need to understand the importance of proper inhibitor levels in the formulation. The use of an oligomer or monomer lot with incorrect inhibitor levels can cause problems ranging from gelation to slow cure rates. Some formulations include the use of additional inhibitors to increase the shelf life of the product. In a few instances, the inhibitor level is adjusted for the time of year, shipping conditions and location of the plant. Remember material shipped in the Southwest in the middle of summer can achieve temperatures in excess of 100° C in a non-air-conditioned truck.

The use of an outside training program is often desirable, since it can reveal blind spots in the in-house program as well as provide contacts for troubleshooting which may be needed down the road. RadTech International periodically conducts such courses for the industry.

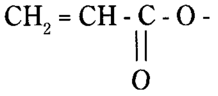
Appendix One

GLOSSARY OF TERMS

ABRASION RESISTANCE
The ability of a material to withstand mechanical action such as rubbing, scraping or erosion, that tends to progressively remove material from the surface.

ACCELERATION
Increasing power or energy of electrons through an electrical field (usually 50 to 350,000 volts or more) in a vacuum.

ACRYLATES
Chemical materials, usually monomers and oligomers, which contain the grouping:



$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-$$

ACTINIC RADIATION
Electromagnetic radiation capable of producing photochemical action, but of insufficient energy to produce ions in a medium of common materials. Usually having a wavelength of greater than 185 nanometers.

ACUTE TOXICITY
Relates to short term, generally single dose exposure to toxic or potentially toxic materials. Common tests in this class include skin and eye contact, ingestion, or inhalation. Observation periods are typically not longer than 14 days.

ADHESION
The state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both.

ADHESIVE
Any substance that is capable of bonding other substances together by surface attachment.

AROMATIC KETONE
A group of chemical materials most of which are sensitive to light and readily form free radicals. The structure is ArCOR (Ar). Some of these are useful photoinitiators.

BENZOIN ETHER
A group of chemical materials most of which are sensitive to light and readily form free radicals. Chemical structure is ArCOCHORAr. Some of these are useful photoinitiators.

BOND STRENGTH
The strength of the union between materials.

CATIONIC (IONIC) CURE
A cationic reactive species generated from a stable molecule by energy absorption which initiates polymerization of cationically sensitive monomers such as epoxides.

CHRONIC EXPOSURE
Long term repeated exposure of a test chemical (two years or more) useful for the purpose of evaluation of carcinogenic potential.

CHRONIC TOXICITY
Relates to long-term toxic effects of repeated exposure to chemical substances.

CONTROLLED AREA
An area to which access is controlled by the users for purposes of safety.

CROSSLINKING
The chemical combining of monomers, oligomers and/or polymers to enhance their properties which also renders them insoluble.

CURE
Conversion of a material from a raw state to a finished and useful condition by chemical reaction.

DARK REACTION
Reactions which take place in closed containers of UV/EB curable formulations — usually premature polymerization.

DEFOCUSED SYSTEM
A curing system in which the substrate is positioned either closer to or farther away from the lamp than the focal distance.

DERMATITIS
Inflammation of the skin which may be evidenced by itching, redness, and skin lesions.

DOPED LAMPS
The specific wavelengths emitted from an ultraviolet lamp are mainly dependent upon the fill. Using mercury as the norm, the spectral output can be changed by the addition of dopants such as beryllium or iron.

DOSE
Energy absorbed per unit mass usually in Megarads. One Megarad equals 1 million rads, 10^8 ergs/g, 2.39 calories/g, 4.3 BTU/lb., 10 Watt-seconds/g or 4.54 kW seconds/lb.

DOSE RATE
Dose per unit time, usually Mrads/second.

DOSE-RESPONSE RELATIONSHIP
Relationship between the amount of exposure and the observed effect(s) upon the material.

DOUBLE BOND
A type of chemical bond wherein two pairs of electrons are shared between two atoms.

EDEMA
A condition of body cells, tissues, or serous cavities containing abnormal amounts of fluid.

ELECTROMAGNETIC SPECTRUM
The entire range of wavelengths of electromagnetic radiation, extending from gamma rays to the longest radio waves and including microwave, ultraviolet, visible and infrared.

ELECTRON
An electron is a negatively charged particle with a mass of 9.21 x 10^{-28} grams.

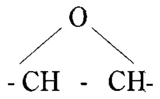
ELECTRON BEAM
A beam of electrons displaced from a metallic filament by a high voltage source of acceleration.

ELECTRON CURTAIN
An electron beam generated via a linear source (or cathode), as opposed to a scanned source.

ELECTRON PENETRATION
The depth of penetration into a substrate by the accelerated electrons. Depth of penetration depends on the kinetic energy imparted to the electron by the accelerating voltage.

ELEMENT
The basic unit of matter.

EPOXY GROUP
A reactive part of a chemical molecule with structure:



ERYTHEMA
Any redness of the skin, as in a sunburn.

FILM BADGE
A small device which contains a radiation sensitive film. It is used to monitor personnel when working in areas where possible exposure to radiation exists.

FLASH POINT
The temperature in degrees °F (°C) at which a liquid gives off sufficient vapor to form a flammable or ignitable mixture with air.

FLASH XENON (PULSED XENON)
Lamp containing xenon gas which produced UV radiation using a special electric transformer system.

FLEXIBILITY
The ability of a material to twist and bend.

FOCAL DISTANCE
The distance from a lamp assembly at which the peak energy can be obtained.

FREE RADICAL
A reactive species having an unpaired electron which initiates a reaction with a double bond, e.g., acrylic polymerization. It is produced from its stable paired state by energy absorption.

FREE RADICAL REACTION
A chemical reaction which takes place only when a free radical or molecule which has lost one electron is generated.

FUNCTIONALITY (WITH REFERENCE TO CHEMICAL REACTION)
The number of groups on any one molecule which can readily react.

GLOSS
The property of a surface which causes it to reflect light.

HAZARD
Refers to the likelihood that a substance or process will cause injury in a given set of conditions of manufacturing, use or disposal.

HEAT CURE (THERMAL CURE)
A curing reaction which takes place when the materials are subjected to a form of heat.

INERT ATMOSPHERE
The blanketing (usually from air) by a nonreactive gas (usually nitrogen, sometimes a mixture of nitrogen and carbon dioxide).

INDUSTRIAL HYGIENE
Science which addresses the recognition, evaluation and control of factors or conditions in the industrial environment which may cause occupational disease.

INFRARED ENERGY
Photon energy having wavelengths between 1 and 100 microns.

INITIATION
The first step in a crosslinking process.

IONIZING RADIATION
Particle or electromagnetic energy capable of producing ions in common materials; usually energies of greater than about 10 electron volts or 16×10^{-19} joules.

LEL (LOWER EXPLOSIVE LIMIT)
Refers to the lowest concentration of gas or vapor (percent by volume in air) which will burn or explode if ignited.

LINE SPEED
The rate of travel of the substrate under the electron beam or UV lamp, usually expressed in meters or feet per minute.

LINEAR CATHODE OR LINEAR SOURCE
See electron curtain.

MAR RESISTANCE
The ability of the surface of a material to withstand mechanical forces.

MEGARAD
Unit of absorbed energy equal to 10 joules or 2.39 calories per gram. A commonly used term describing dose in electron curing equal to one million rads.

MEGAVOLT OR MeV
A megavolt is one million electron volts. This is the kinetic energy acquired by an electron accelerated across a potential of one million volts (1,000,000 volts).

MERCURY LAMP
Lamp in which light is generated through presence of mercury vapor. Most UV lamps are mercury vapor lamps.

MICROWAVE
Energy having wavelengths between 1 and 10 millimeters.

MONOMER
A molecule of relative low molecular weight and simple structure capable of combining with itself or other similar molecules through reactive sites to form polymers.

MSDS (MATERIAL SAFETY DATA SHEET)
A document, available from suppliers of chemical products, which outlines potential hazards associated with the particular chemical product and methods for proper handling.

MUTAGEN
A substance which causes genetic change.

NANOMETER
A unit of distance commonly used in measuring wavelength in the electromagnetic spectrum — one billionth of a meter (10^{-9} meter).

NITROGEN BLANKETING
The practice of using nitrogen gas to exclude air from the surface of the product to be cured during radiation processing.

OLIGOMER
A lower molecular weight resin or polymer which is used in a radiation curable formula.

OXYGEN INHIBITION
The effect of oxygen which terminates or retards the rate of polymerization.

OZONE
A different form of oxygen that occurs when high energy electrical discharge is present(O_3).

PERCUTANEOUS
Absorption through the skin.

PHOTOINITIATOR
A molecule which when exposed to a specific wavelength of energy forms a reactive species which starts the chain reaction to cause polymer formation.

PHOTON
Radiant energy viewed as bundles of energy.

PHOTOSENSITIZER
A chemical which will transfer energy and form free radicals by interacting with another chemical.

PHOTOPOLYMER
A composition which will either crosslink or depolymerize on exposure to light, forming a physical differentiation between the exposed and unexposed portion.

POLYMER
A macromolecule consisting of a large number of monomer units. The molecular weights may range from about 20,000 into the millions.

POLYMERIZATION
A chemical reaction usually carried out with a catalyst, heat, or energy in which two or more relatively simple compounds or molecules combine to form a macromolecule.

POST CURE
Continuation of reactions of materials in the ink or coating after exposure to radiation has ceased.

PRIMARY IRRITATION INDEX
A numerical measure of the skin irritancy of a substance. The sum of the erythema and edema scores at 24 and 72 hours over abraded and intact skin divided by two. The Draize score.

PROPAGATION
The continuation of the crosslinking process.

QUARTZ TUBE
A lamp made from a silicate material called quartz which is fitted with electrical connections to form an irradiator. It may be made into an infrared emitter or it may be filled with mercury vapor to produce ultraviolet light.

RAD
The unit of dose equal to an energy absorption of 100 ergs per gram.

RADIANT ENERGY TRANSFER
The transfer of energy directly from a source without any intervening means of conveyance — in contrast to conduction through wires or convection by a gaseous intermediate, i.e., hot air.

REACTIVE DILUENT
A chemical which serves two purposes in a formulation: thinning or viscosity reduction and providing reactivity with other ingredients for curing or polymerization.

RESIN
A polymeric material, either natural or synthetic, which is usually considered an ingredient in formulation.

RISK
Refers to the expected frequency of adverse effects resulting from exposure to a substance or process. Judgments of risk can be made qualitatively by relating effects seen in an exposed population to those seen in an unexposed population. This is relative risk. Absolute risk is the excess risk due to a given exposure.

SAFETY
Refers to the practical likelihood that a substance will not cause injury in a given set of conditions of manufacturing, use or disposal. (There is no such thing as absolute safety since there may always be a dose or exposure to a substance which may result in a finite hazard.)

SENSITIZATION
Process in which an exposed human or animal has an exaggerated (allergic) response upon re-exposure to a chemical substance.

SHELF LIFE
The amount of time a material may be stored under specified conditions with no significant changes in properties.

SOLVENT
A substance capable of dissolving another substance to form a uniform, dispersed mixture at the molecular or ionic level.

STABILIZERS
Additives to coating, ink or adhesive formulations which help extend shelf life and resist heat or other degradation.

SUBCHRONIC EXPOSURE
Repeated or continuous exposure to a chemical for periods of 2 to 26 weeks at low concentrations.

TERATOGEN
An agent or factor that causes abnormal fetal development.

TERMINATION
The completion of the crosslinking process.

THRESHOLD LIMIT VALUE (TLV®)
This is the airborne concentration of the substance, which represents the conditions under which it is believed nearly all workers may be repeatedly exposed day after day without adverse effect or discomfort (8 h/day: 40 h/week). Because of the physiological differences among various workers, there may be a small percentage of individuals who will be affected at lower concentrations; as well as a small percentage who will show more serious effects because of aggravation of a pre-existing condition. TLV is the registered trademark of American Congress of Governmental Industrial Hygienists.

THROUGH CURE
The curing of the bulk of a material down to and including the material/substrate interface as opposed to a surface cure where only the material/air interface is cured.

TOXICITY
General capacity of a substance to cause injury to a living organism but cannot really be defined without reference to exposure dose, the method of exposure, how often exposure takes place, the specific type and severity of injury, and time needed to produce the injury.

TOXICOLOGY
Term is used here in the broadest frame of reference, namely, the collection of disciplines which evaluate and characterize the biological effects of chemicals, products, and processes in man, animals, plants, and lower organisms.

ULTRAVIOLET LIGHT
Radiant energy in the wavelength band of 180 to 400 nanometers (1.8 to 4.0 x 10^{-7} meters).

UNSATURATION
A double bond in a chemical molecule (usually between carbon atoms or between carbon and another atom) which is reactive to free radical initiation.

VISCOSITY
The internal resistance to flow exhibited by a fluid.

VOLATILES
Solids or liquid materials which pass into the vapor state at a given temperature.

WATTAGE
The intensity of energy output. For electron beams, ***wattage = voltage x amperage.***

WINDOW
A metallic foil in an electron beam generating unit that allows passage of energetic electrons from the beam.

X-RAY
Electromagnetic energy in the wavelength range of about 0.1 to 10 nanometers, generated when energetic electrons are stopped in matter. X-rays are the major environmental hazard associated with electron accelerators.

Appendix Two

INDEX OF ARTICLES IN *RADTECH REPORT*

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- Vinyl Ether Functionalized Urethane Oligomers: An Alternative to Acrylate Based Systems — Lapin, Stephen C.

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- Radiation Curing in Japan — Tabata, Yoneho
- Radiation Curing in China — Teh, Ma Zue, Qi, Yan & Jun, Xu Mao

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- Direct and Indirect Methods for the Characterization of Photoinitiator Efficiency — Wehner, G., Ohngemach, J. & Merck E.

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- Coatings in the Web Offset Market — Ragin, Howard
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- The Solution is in the Cure — Laughlin, Charles
- Oygen Inhibition: Causes and Solutions — Hanrahan, Michael J.

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- New Microwave Energized Lamp Systems — Stowe, R.E.
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- Radiation Curing of Adhesives — Satas, Don
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- The Electron Beam: A Tool for the '80s (and '90s) — Bradley, Richard
- UV Spells Success for Furniture Manufacturer — Rayball, James
- UV/EB Spray Equipment: Innovations and New Technology
- UV Spray Technology Paves Way at Broyhill

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- Benzophenone: A Uniquely Useful Initiator for UV Curing Applications — Arendt, William D. & Wooten, Willard L.
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- New Developments in UV Curing for the Electronics Industry
- UV-Cured Adhesive Sealants Enhance Process Capabilities in the Electronics Industry — Bilodeau, Michael

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- Willamette Industries Finds Success with UV/EB Curing — Bosch, John, Hetzel, Ted & LeFors, John D.
- UV Curable Coatings Technology in the Wood Industry: Compliance for the '90s — Cox, Randy

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- UV/EB Curing Aids Labels and Adhesives
- Ultraviolet Cure of Epoxyfluorosilicones and Related Systems — Eckgerg, Richard P. & Evans, E. Robert

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- Consideration of Title 21 Federal Regulations: Compliance Specific to Coatings — Peters, Yolanda A.
- Packaging Industry Reflects Yes, No Attitude Toward UV/EB Curing — Rayball, James

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- New Developments in Water-Based UV/EB Curable Resins — Stenson, Paul H.

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- Custom Formulators Manufacture Products "Ready-To-Cure" — Rayball, James
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- Determination of Volatiles in Radiation- Curable Materials: A Proposed ASTM Standard — Rose, Bruce
- Utility Companies Promote the Power of UV/EB Technology — Artemakis, Angelo
- UV Can Decorating at Coors Brewing Co.: A Presentation to the EPA
- UV Coating of Chairs at Lowenstein Furniture Group: A Presentation to the EPA — Wood, Prim

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- UV Flexo Flexes its Muscle — Artemakis, Angelo
- Printing and Laminating of Flexible Films by Using UV Curing — Bolte, Georg & Sengewald, Karl H.

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- Corona Treatment: An Adhesion Promoter for UV/EB Converting — Markgraf, Michael P.
- Surface-Discharge Pulsed Light Source for UV Curing — Schaefer, Raymond B.
- Measuring UV Dosage Is Not Enough for Process Control — Radcliff, Robert D.

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- Customers Drive Raw Materials Research — Artemakis, Angelo
- Recent Developments in Radiation Curing Chemistry — Decker, Christian

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- A Chemist's Notes on Quality and ISO 9000 at DSM Desotech — Schmid, Steve
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