



EPA

TECHNICAL BULLETIN

ULTRAVIOLET AND ELECTRON BEAM (UV/EB) CURED COATINGS, INKS AND ADHESIVES

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ULTRAVIOLET AND ELECTRON BEAM (UV/EB) CURED COATINGS, INKS AND ADHESIVES

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ACRONYMS USED IN THIS REPORT

3D	Three Dimensional
ACGIH	American Conference of Government Industrial Hygienists
AFP	Association for Finishing Processes (an affiliate of SME)
AIM	Architectural, Industrial and Maintenance
ASTM	American Society of Testing Materials
C	Centigrade
CAS	Chemical Abstract Service
CATC	Clean Air Technology Center
CD	Compact Disk
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
cm	Centimeter
cm ²	Square Centimeters
cm ³	Cubic Centimeters
DVD	Digital Video Disk
EB	Electron Beam
EPA	U.S. Environmental Protection Agency
FDA	U.S. Food and Drug Administration
FM	Frequency Modulated
fpm	Feet per minute
Gy	Gray unit of energy absorption, equals one Joule per kilogram
HAP	Hazardous Air Pollutants
hr	Hour
HVAC	Heating, Ventilating and Air Conditioning Equipment
in ²	Square Inches
IR	Infrared
kg	Kilogram
LAER	Lowest Achievable Emission Rate
LEL	Lower Explosive Limit

MBTU	Millions of British Thermal Units
mm	millimeters
MSDS	Material Safety Data Sheets
NCS	New Chemical Substance
NFPA	National Fire Protection Association
nm	Nanometers
NTIS	National Technical Information Service, U.S. Department of Commerce
OSHA	Occupational Safety and Health Administration
P2	Pollution Prevention
PEL	Permissible Exposure Limit
PMN	Premanufacturing Notice
R	Roentgen
REM	Roentgen Equivalents for Mankind
SAMPE	Society for Advancement of Material and Process Engineering
SME	Society of Manufacturing Engineers
T _g	Glass Transition Temperature
TV	Television
TWA	Time Weighted Average
TSCA	Toxic Substance Control Act
UV	Ultraviolet
VOC	Volatile Organic Compounds
WEELS	Workplace Environmental Exposure Levels
Z	Atomic Number

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ULTRAVIOLET AND ELECTRON BEAM (UV/EB) CURED COATINGS, INKS AND ADHESIVES

INTRODUCTION

The use of **ultraviolet** and **electron beam (UV/EB)** cured **coatings, inks** and **adhesives** has increased dramatically over the last decade. Currently, this pollution prevention (P2) technique is used in a wide variety of **coating**, printing and unique product applications. This Clean Air Technology Center (CATC) Technical Bulletin provides basic information on **UV/EB** technology and how it has advanced since the Control Technology Center (CATC predecessor) published "Radiation-Curable **Coatings**" (EPA-600/2-91-035) in 1991.

Increasing numbers of **coating** and printing facilities are using or considering **UV/EB** technology because it is effective and profitable for them to do so. In "**Radiation-Cured Coatings**," three reasons were given for this: (1) a 75-90% energy savings; (2) a 50-75% savings in floor space; and, (3) higher production rates. All three reasons are still valid and the advantages may be even greater today. **UV/EB**-curing units are significantly more energy efficient and compact than thermal drying/curing systems that are used with conventional **coatings, inks** and **adhesives**. Also **UV/EB**-curing is extremely fast - almost instantaneous to a few seconds at most. Because **UV/EB** systems emit only very small amounts of **volatile organic compounds (VOC)**; see Appendix D) and virtually no **hazardous air pollutants (HAP)**; see Appendix E), they generally require no add-on air pollution control equipment and are considered environmentally friendly. In fact, the South Coast Air Quality Management District in California classifies **UV/EB coating** and printing applications as "Super Clean Technology" and has eliminated or minimized air pollution permitting procedures for facilities using this technology.

UV/EB materials cure almost instantaneously when exposed to **UV/EB radiant energy** (i.e., **UV/EB radiation**). Manufacturers of **UV/EB** equipment include shielding and safety interlocks in their equipment that adequately protect workers from exposure to **UV/EB radiant energy**. However, much confusion exists concerning worker safety. The term "**radiation**" has been applied to many different types of energy sources that individually present significantly different health and safety issues. For example, the term has been applied to nuclear **radiation**, **radioactivity**, solar **radiation**, **UV radiation**, **EB radiation**, microwave **radiation**, fluorescent lamp **radiation**, computer monitor **radiation**, television (TV) set **radiation**, TV and radio broadcast **radiation**, and even illumination radiating from incandescent lamps. The unifying attributes in all of these "**radiation**" sources are that energy (in some form) is emitted from a source, propagated radially along a line-of-sight, and absorbed. However, the effects of these various forms of "**radiation**" on humans are very different and depend on the type and source of the energy. Because over-use and misuse of the term "**radiation**" has and continues to cause confusion, we will use the term "**UV/EB radiant energy**" to describe the "**radiation**" that cures **UV/EB** material. See the **UV/EB Radiant Energy** section of this report for more detailed

information on that topic. Additional information can be found in Appendix A, **Ultraviolet and Electron Beam Radiation vs. Radioactivity**.

When we refer to **UV/EB** material in this Technical Bulletin we are speaking of **UV/EB-cured coatings, paints, inks, adhesives**, and similar products in general. We use the name of the specific type of material (e.g., **coating, ink**, etc.) when information pertains to only that material. Trade-names are not used because they are not descriptive of the chemistry of the materials involved and might be misconstrued as a recommendation.

To fully understand and appreciate **UV/EB** technology and its advantages we need to consider organic chemistry, physics, engineering, manufacturing processes and cost accounting. This Technical Bulletin tries to bring all of these perspectives together.

BACKGROUND

Use of radiant energy cured **coatings** dates back at least 4,000 years. Ancient Egyptians used a type of **UV coating** that cured when exposed to sunlight in preparing mummies (AFP/SME, 1986)³⁰ Also, an asphalt-based oil **coating** that polymerized upon exposure to solar **radiation** was used by ancient Egyptians as a sealant for ships (Decker, 1987).³⁰

In the modern era, scientific interest in developing **UV/EB-cured** systems began in the 1940's. At that time, the first patent was granted for an unsaturated polyester styrene printing **ink** that polymerized under **UV** exposure. One of the first attempts at applying **UV/EB-cured** systems to manufacturing was made in the late 1960's, but successful commercial application did not evolve until the early 1970's. The publicized driving forces behind development of commercially viable systems were the energy crisis of 1974 and growing environmental concerns about **VOC** emissions resulting from conventional thermal-cure systems. However, the primary motivations for use of **UV/EB-cured** systems were and still are improved product performance and increased productivity.

Early applications of **UV/EB-cured** systems were limited to flat sheets, mainly in the wood products and printing industries. Radiant energy cured processes of that time were limited by the need for a line-of-sight energy source. Starting in 1974, **UV-curable inks** and varnishes were used for decorating aluminum beverage cans. Improvements in plant engineering, such as rotating conveyors, multiple **UV** sources and adjustments to curing equipment, have allowed **three-dimensional (3D)** applications of **UV/EB-cured** materials. In addition, advances in **polymer** science have provided a wide variety of **UV/EB-cured** materials that can exhibit characteristics required by the end-user in specific applications.

PART I: THE BASICS

This section summarizes basic information on **UV/EB** materials, including their use and application. A more comprehensive discussion of important technical, safety and regulatory issues is presented in “PART II: THE DETAILS” section of this report. A number of terms are introduced that may not be familiar to you. To help you, a glossary of terms is provided at the end of this report. Terms included in the glossary are in **BOLD** print within the body of the report. Acronyms also are used for many terms or complex names. A list of acronyms is provided at the front of this report, immediately after the table of contents.

WHAT ARE UV/EB-CURED MATERIALS?

UV and **EB** materials cure (polymerize) when exposed to **UV** and **EB radiant energy**, respectively. Virtually all components of a **UV/EB** formulation become a solid part of a cured **coating, ink** or **adhesive**. Generally, only small amounts of **VOC** may be emitted. For **UV/EB** materials, curing means the interaction of liquid molecules (**monomers, oligomers** and **photoinitiators**) to form **polymers**. This curing process is known as **polymerization**. It forms long molecular chains that are the carbon backbone for a **polymer** molecule. After **polymerization** the **UV/EB**-cured material is a solid, consisting of pigments and **polymer** molecules that may be tangled together and interconnected by crosslinks.

Conventional **VOC/solvent** borne and waterborne **coatings, inks** and **adhesives** use thermal energy to evaporate volatile components (i.e., organic **solvent/VOC** and/or water) and to cure. As a result, most of the volatiles in a conventional **coating, ink** or **adhesive** are emitted to either a control device or the atmosphere. Only the remaining non-volatile part in a conventional material actually cures to form a final **coating, printing** or **adhesive** that remains on a **substrate**. Some degree of **polymerization** may take place in the cure of a conventional material. The amount of **polymerization** that occurs during the cure of a conventional material (as opposed to **polymerization**/prepolymer formation that occurs during the paint/**ink/adhesive** manufacturing process) varies depending on the type of material. For example, virtually no **polymerization** occurs when curing a conventional lacquer; however, **polymerization** would be a critical process when curing a conventional urethane, epoxy, or acrylic.

Since you are probably more familiar with conventional **coatings, inks** and **adhesives** and how they are used, it may be helpful to compare **UV/EB** materials to conventional materials. So, we will spend a little time here reviewing how conventional **coating, ink** and **adhesive** systems work before elaborating on **UV/EB coatings, inks** and **adhesives**.

Review of Conventional Coatings, Inks and Adhesives

Conventional oil/**solvent** based and waterborne **coatings**, **inks** and **adhesives** are evaporative systems. They use suitable partially pre-polymerized **monomers** (alkyd, acrylic, epoxy, silicone, etc.) and pigments dispersed in a **solvent**. These pre-polymers must further polymerize and cross-link during the cure to become solids.

Conventional pre-polymers are formed by a chemical condensation reaction at elevated temperatures. This reaction occurs at a chemical plant or **coating**, **ink** or **adhesive** manufacturing facility, and not during the cure. Just before the **pre-polymer** gets long enough to form a gel, the temperature is reduced and the pre-polymer is dispersed in either an organic **solvent** or water. The organic **solvent** is usually **VOC** and often accounts for more than half of the volume of liquid **coating**. Water accounts for a similar fraction of the volume of water-based **coatings**. Some conventional **coatings** even contain **HAP**.

When conventional materials are applied and the organic **solvent** or water evaporates, pre-polymerized **resin** molecules are able to contact each other. Solidification of the **coating** occurs as the pre-polymer further proceeds in its **polymerization** by a chemical reaction. This is a relatively slow process because the temperature is now much lower than it was in pre-**polymerization** and, in fact, it is a process that never ends. You may have observed that conventional paints thicken in storage (even without evaporation), change their surface finish and shrink over a period of years.

For lacquers, **solvent** can be much more than half of the final volume of **coating** as applied. Lacquers simply solidify upon evaporation of the **solvent**. They are more fully polymerized during their manufacture than other conventional **coatings** and no further **polymerization** is needed when they are applied. However, there is no **crosslinking** and they melt or mar easily. They shrink from loss of **solvent** and not because of further **polymerization**.

Conventional materials must be applied with sufficient air flow (ventilation) to keep the **solvent** concentration in air below a quarter of the Lower Explosive Limit (LEL). This is required by the National Fire Protection Association (NFPA) and the Occupational Safety and Health Administration (OSHA). For spray applications, air flow of either 100 feet per minute (fpm) or 60 fpm (for electrostatic deposition) through the area in which vapors are generated is required. In addition to explosion/fire safety issues, there also are health effects issues for humans that breathe **solvent** vapors.

Conventional materials use **infrared (IR) radiant energy** (i.e., heat) to cure. **IR** energy is emitted naturally from everything. It is electromagnetic **radiation** with a wavelength between 1000 nm and 11,000 nm. Visible light is electromagnetic **radiation** with wavelengths from 400 nm to 700 nm. Microwaves are electromagnetic **radiation** with wavelengths in meters (See Figure 1). **IR** energy is sensed as radiant heat and its wavelength is based upon temperature. Heat is used to evaporate organic **solvent** or water and to accelerate **polymerization**.

At ambient temperatures, evaporation and **polymerization** can take from hours to days. Thermal ovens can reduce evaporation and **polymerization** time to minutes. However, thermal ovens are bulky, take up considerable floor space, and consume large amounts of energy because they must heat the air flow through the oven, in addition to heating the **coating, ink, or adhesive** and **substrate**.

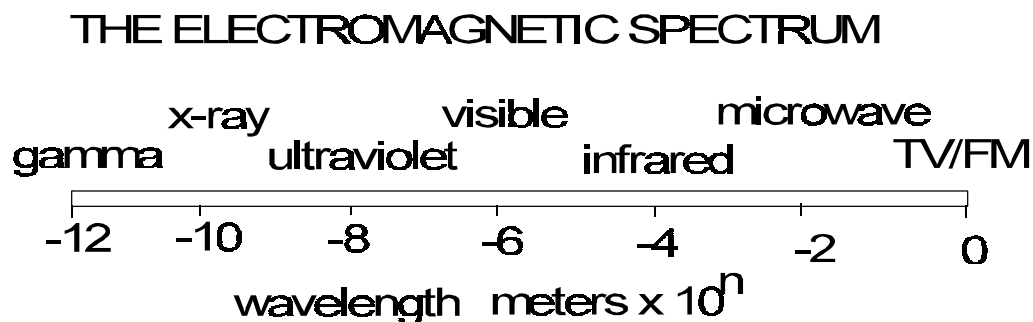


Figure 1: General Domains of the Electromagnetic Spectrum from Gamma Radiation to Television and Frequency Modulated (FM) Wavelengths

UV/EB-Cured vs. Conventional Coatings, Inks and Adhesives

UV/EB materials consist of pigments and the same **monomers** and **oligomers** that react to form **polymers** in conventional **coatings**, but without being subjected to pre-polymerization. **Oligomers** are created by joining about 3 to 5 **monomer** molecules, but this is not to be confused with pre-polymerization. Acrylic groups or vinyl ether groups are reacted with **monomer** and/or **oligomer** molecules in a UV/EB material, and become side-branching or pendant groups to the carbon backbone. These are referred to as **functional groups** because they are more reactive and, therefore, require less increase in energy to polymerize **monomers** and **oligomers**. In addition, they are used to achieve desired properties and **crosslinking** between **polymer** chains.

Polymerization is actually a chain reaction, in which **monomers** or **oligomers** are added to a backbone of carbon atoms. Each **monomer** or **oligomer** molecule is added as another link in the chain, or as another vertebra in the carbon backbone. A **polymer** chain can be thousands of **monomer** or **oligomer** molecules in length.

For **UV/EB** materials, **polymerization** actually is initiated by a compound included in the formulation called a **photoinitiator**. A **photoinitiator** absorbs **UV/EB radiant energy** and either forms **free radicals** or cations and anions. Until a **photoinitiator** receives **UV/EB radiant energy**, a **UV/EB-cured** material does not have enough energy to initiate and complete **polymerization**. Upon absorbing the **UV/EB** energy, **photoinitiator** molecules have enough energy to split into either **free radicals** or cations and anions. These **free radicals** and cations are energetic enough to create a **polymer** from **monomers** and **oligomers**.

Free radicals produce a very fast reaction that occurs almost immediately and, for all practical purposes, reaches completion. This results in a finished (cured) **coating, ink** or **adhesive** that is almost completely polymerized and nearly ceases to polymerize further. Only trace quantities of **monomers, oligomers** and **photoinitiators** remain trapped within the **polymer** after a **free radical** reaction. These trace quantities may react with each other over time as they diffuse through the **polymer**. However, this occurs very slowly.

When cations (**Bronsted** or **Lewis acids**) are formed, they generate more ions by spontaneously breaking other **photoinitiator** molecules. These cations also initiate **polymerization** that can spread, even in the absence of **UV/EB radiant energy**, after a **UV/EB-cured** material has received enough radiant energy to start **polymerization**. These **cationic photoinitiators** cause **polymerization** to occur somewhat more slowly; i.e., **polymerization** occurs in seconds. On the other hand, being a chemical process, **cationic polymerization** can be completed in the dark (without **UV/EB radiant energy**) once it has started.

In 1991, **UV/EB** materials used volatile components, but these are no longer needed or used. **UV/EB** materials rarely use **solvents**. The only exception is to reduce viscosity and allow application of a thinner coat (usually with **adhesives**) or to facilitate spray **coating**. Even when a **solvent** is used with a **UV/EB** material, the amount of **solvent** and, therefore, the amount of **VOC** emissions are generally much less than from conventional materials. In the typical case where no **solvent** is used, only cure volatiles between 1-10% of the applied film weight might be emitted. Usually cure volatiles are less than 5%. At this level, uncontrolled emissions are no worse than that of a conventional operation equipped with very good emission capture and control technology. However, no control technology is either needed or used with **UV/EB** materials.

WHERE ARE UV/EB-CURED MATERIALS USED?

UV/EB coatings, inks and **adhesives** are used in a variety of applications such as printing **inks**, overprint varnishes, release **coatings**, primers, pigmented paints, clear topcoats, bonding **coatings** for magnetic tape, bonding for abrasives, encapsulates, pressure sensitive **adhesives**, and permanent bond **adhesives**.⁵ The list of applications keeps growing; therefore, any static list of applications should not be expected to be complete. However, in order to appreciate the extent to which **UV/EB** technology is being applied, a list of **UV/EB** applications compiled from

Envirosense ¹⁴ and the RadTech **UV/EB**-Curing Primer ²³ is provided in Table 1. Examples of **UV/EB** material applications can also be found in Appendix B.

TABLE 1: UV/EB COATING, INK AND ADHESIVE APPLICATIONS	
INDUSTRY	APPLICATION
AIM Coatings (Architectural / Industrial / Maintenance coatings applied to protect from corrosive environment)	metal and concrete structures pipes tanks processing equipment
Aircraft	primers color coats topcoats
Automotive Parts	underbody paints primers color coats topcoats refinishing
Coil Coating	Applied to coiled sheet metal that is used in: household appliance industries transportation industries construction industries container industries
Dental	fillings
Electronics	microelectronics photomasks solder masks notations on circuit board encapsulation of circuits or components optical fiber coatings compact disks (CDs) digital video disks (DVD's)
Flexible Plastics	decals decorative laminates shrink film magnetic recording media abrasive films release films

TABLE 1: UV/EB COATING, INK AND ADHESIVE APPLICATIONS	
INDUSTRY	APPLICATION
Highway	coatings used to mark lanes coatings used to provide directional arrows on roadway
Leather	finishes topcoats
Machinery and Equipment	farm equipment construction equipment electrical machinery heating, ventilating, and air conditioning systems (HVAC) industrial machinery computers office equipment
Marine	ships offshore platforms other steel and aluminum structures
Metal containers	beverage cans lids and closures food cans
Optics	eyeglass lenses optical fibers
Paper and Paperboard	record albums folding cartons juice cartons magazines paperback books business forms bank notes and money release paper abrasive coated paper
Rigid Plastics	vinyl floor covering and tiles bottles credit cards sports equipment medical equipment

TABLE 1: UV/EB COATING, INK AND ADHESIVE APPLICATIONS	
INDUSTRY	APPLICATION
Textiles	sizing fill coats topcoats
Wire	magnet wire
Wood Furniture	furniture kitchen cabinets doors trim moldings
Wood Products	hardboard panels plywood panels particle board panels hardwood flooring door laminates

DO UV/EB FORMULATIONS USE CONVENTIONAL RESINS?

All **coatings, inks and adhesives** (i.e., **solvent** borne, waterborne, or **UV/EB-cured**), regardless of curing method, use basically the same **resins**. However, the **resins** used with **UV/EB-cured** material have been modified by including **functional groups** and **photoinitiators** that trigger **polymerization**. For **UV/EB** materials, different performance properties have been gained by using acrylics, methacrylates, epoxies, polyesters, polyols, glycols, silicones, urethanes, vinyl ethers, and combinations of these. Structurally different **monomers** or **oligomers** may be blended together to adjust properties of a final **polymer**. The composition of a formulation is usually considered proprietary and, therefore, is usually referred to by a trademarked name which does not normally reveal its composition. Table 2 shows **monomers** and **oligomers** that were available in 1991. Either acrylic or vinyl ether **functional groups** are included in these **monomers** to enable them to be cured by **UV/EB radiant energy**.

The list of **monomers** and **oligomers** has grown to be quite large in 1999. See Table 3. This listing is by generic types. Actual formulations are composed of these types of compounds in a proprietary mix. The mix will be identified by a trademarked name that will give no clues as to constituents.

Table 2. RADIATION-CURABLE MONOMERS IN 1991 ³⁰

SYSTEM	REACTIVITY	OXYGEN INHIBITION	DURABILITY	EB CURABLE	UV CURABLE
Polyester/styrene	Low	High	Poor	No	Yes
Acrylates	High	High	Moderate	Yes	Yes
Thiol-polyene	High	Low	High	Yes	Yes
Cationic Epoxies	Medium	Low	Fair	No	Yes

Source: Decker, C. "UV-Curing Chemistry: Past, Present, and Future", J. of **Coatings Tech.**, 1987
Vrancken, A. "Market Trends for Irradiation Curable **Coatings** in Europe", **Radiation Curing V**,
Association of Finishing Processes of SME, Boston, 1980

HOW ARE UV/EB MATERIALS CURED?

UV/EB materials cure (change from a liquid to a solid) by a reaction that involves both **polymerization** and **crosslinking**. UV-cured materials need **UV radiant energy** to polymerize **monomers** and **oligomers** into a solid. EB-cured materials need **EB radiant energy** to polymerize **monomers** and **oligomers** into a solid. There are many **polymerization** mechanisms; however, currently only two **polymerization** mechanisms are used for curing UV/EB materials: **free radical polymerization** and **cationic polymerization**. A **free radical** cured UV material must be either very thin, clear, or both in order to let sufficient amounts of **UV radiant energy** to (del) penetrate all the way through the material. A **free radical** cured EB material can be filled, pigmented and thicker because **EB** penetrates more than **UV**. **Cationic photoinitiators**, after UV/EB exposure, spontaneously form cations that trigger further **cationic polymerization**. Once the **cationic polymerization** has been started, **cationic** reactions can carry **polymerization** to completion in thicker, opaque materials, or even in the dark (i.e. after radiant energy exposure stops).

In **free radical polymerization**, a **monomer** or **oligomer** joins with a **free radical** and, in effect, forms a larger **free radical**. This larger **free radical** then acts upon another **monomer** or **oligomer** and forms an even larger molecule, and so on. The process is a chain reaction (another term used by chemists and physicists to mean a continuing reaction), that is endless until a **polymer** molecule is terminated. Termination occurs when one **polymer** chain runs into the end of another **polymer** chain, an oxygen atom reacts with the end of a chain, or a **polymerization** becomes so nearly complete that further reactants are not available.

Table 3. FAMILIES OF RADIATION-CURABLE MONOMERS IN 1999

Acrylated Aliphatic Oligomers	Cycloaliphatic Epoxides
Acrylated Aromatic Oligomers	Cyclohexyl Methacrylate
Acrylated Epoxy Monomers	Ethylene Glycol Dimethacrylate
Acrylated Epoxy Oligomers	Epoxy Methacrylates
Aliphatic Epoxy Acrylates	Epoxy Soy Bean Acrylates
Aliphatic Urethane Acrylates	Glycidyl Methacrylate
Aliphatic Urethane Methacrylates	Hexanediol Dimethacrylate
Allyl Methacrylate	Isodecyl Acrylate
Amine-modified Oligoether Acrylates	Isooctyl Acrylate
Amine-modified Polyether Acrylates	Oligoether Acrylates ,
Aromatic Acid Acrylate	Polybutadiene Diacrylate
Aromatic Epoxy Acrylates	Polyester Acrylate Monomers
Aromatic Urethane Methacrylates	Polyester Acrylate Oligomers
Butylene Glycol Acrylate	Polyethylene Glycol Dimethacrylate
Silanes	Stearyl Methacrylate
Silicones	Triethylene Glycol Diacetate
Stearyl Acrylate	Vinyl Ethers

Note: These **monomers/oligomers** were cataloged in 1999. These can be blended to achieve desired properties. These can be combined with any of a similar number of types of **photoinitiators**. The **photoinitiators** tend to be aromatic molecules that are more sensitive to **UV** or **EB** than the **monomers** and **oligomers** are.

Cationic polymerization is an ionic process that is not inhibited by oxygen and, therefore, can cure in air without a **nitrogen blanket**. **Cationic polymerization** will continue after exposure to **UV/EB radiant energy** source ceases. Therefore, the only concerns are to initiate **cationic polymerization** and to store the product for a few seconds to allow for the cure to complete.

UV/EB monomer and an **oligomer** molecules have **functional groups** that attach to the side of a carbon chain. These also are referred to as pendant groups. Pendant groups aid in reducing the energy that must be added to polymerize and to form crosslinks. Crosslinks interconnect carbon chains and, as a result, provide greater mechanical strength, resistance to abrasion, higher softening temperatures, and increased mar resistance.

Polymerization and **crosslinking** are the critical processes that take place as a **UV/EB** material cures. **Free radical** curing is very fast and may reach completion in a millisecond or less. **Cationic** curing is slower and may take a few seconds to reach completion. Fortunately, cations are more stable than **free radicals** and endure much longer.

Monomer and **oligomer** molecules are initially short enough to be mobile and, therefore, are in a liquid state. As **polymerization** progresses, **polymer** chains grow in length, become less mobile, and form a gel. In the gel state, a **polymer** solidifies, but has no significant mechanical strength. As **polymerization** continues, **crosslinking** occurs and the **polymer** gains mechanical strength. A material is fully cured when **polymerization** and **crosslinking** processes are virtually completed.

DO UV/EB-CURED MATERIALS NEED SPECIAL EQUIPMENT?

For the most part, the same equipment that is used to apply conventional **coatings, inks** and **adhesives** can be used to apply **UV/EB**-cured materials, although they may be adjusted differently. The only major difference is how these materials are cured.

Curing Units

UV-curing units contain one or more **UV** lamps, a reflector for each lamp, a means of dissipating heat from the lamps (which may be ventilating air flow), and shielding to protect people from exposure to **UV**. All **UV**-curing unit manufacturers now include shielding as an integral part of a curing unit.

An **EB**-curing unit contains an **electron beam** generator and shielding to attenuate **x-rays** that are generated during the curing process. An **EB**-curing unit is heavier and larger than a **UV**-curing unit because it has more massive shielding to absorb **x-rays**. All **EB**-curing unit manufacturers include such shielding as an integral part of a curing unit.

For both **UV/EB**-curing units, production rates are determined by the composition and applied thickness of the **UV/EB**-cured material, intensity of radiant energy in the curing unit, and amount of radiance that is absorbed. **UV/EB** materials cure almost instantaneously to within a few seconds when exposed to the appropriate radiant energy. Compared to thermal dryers used with conventional **coating, ink** and **adhesive** applications, **UV/EB**-curing units provide for a 75-90% savings in energy, 50-75% savings in floor space, and higher production rates.

By contrast, for conventional **coating, ink** and **adhesive** applications, a thermal oven is used to flash off organic **solvent** or water and to harden/cure the applied material enough for handling. The oven is insulated to minimize heat loss (other than to the air flow that passes through it). Air flow through a thermal oven must assure that the concentration of organic **solvent** does not exceed one fourth of the LEL. Production rates are determined by the composition and applied

thickness of the conventional material, path length through the thermal oven, temperature, and air flow. Oven temperature, air flow, oven size, and production rate are inter-related factors in conventional processes. The temperature must be high enough to evaporate the **solvent** or water and to harden the **coating** enough for handling, but must not damage the **substrate** or the **coating**. Air flow must remove and dilute **solvent** vapors to prevent excess concentrations from occurring. The size of the oven is based upon the time required to dry, harden, and/or cure a conventional **coating, ink** or **adhesive** at the desired production rate.

Printing and Roller Coating

Although printing presses and roller coaters that use **UV/EB** materials may differ in detail, they are essentially the same as those that use conventional materials. The differences are mainly due to the location, size and speed of the curing unit. For printing, **UV/EB**-curing units are often mounted on a printing press after the application of each color. For roll-**coating**, the **UV**-curing unit is a chamber with **UV** lamps arrayed to give the desired cure.

Rollers and print transfer surfaces for **UV/EB** material applications can be identical to those used for conventional **coatings, inks** and **adhesives**. **UV/EB** material losses only occur when colors are changed, mist is emitted, or a roller must be cleaned. If a roller and its pan are covered to prevent **UV/EB radiant energy** from reaching them, a **UV/EB coating** will not cure on or in them. As a result, a roller and pan used with **UV/EB** materials can be left for over a weekend and used again without cleaning. This can minimize both the loss of **UV/EB** material, as a result of cleaning and use of cleaning **solvents** that might be **VOC**.

Spray Painting

For spray **coating**, the same spray paint guns and related equipment used for conventional **coatings** can be used for **UV/EB coatings**. Techniques for spraying viscous **UV/EB** paints include: increased pressure to drive paint through spray gun nozzles; dilution with organic **solvent (VOC)**; dilution with water; or, some combination of heated spray paint guns and these techniques. Viscosity in new **UV/EB** spray paints has been reduced, but still is higher than that typically used for conventional paint spraying. **Reactive diluents** (i.e., **diluents** that become part of the cured **coating**) reduce viscosity and are less toxic and volatile than they once were. However, because **UV/EB** paints tend to be more viscous, heated spray guns may be needed to bring **UV/EB** paint viscosity close to that of conventional paints. New **UV/EB coatings** significantly reduce or eliminate **coating** decomposition, fumes, and/or smoke aerosol problems experienced in the past when using heated spray guns. If used, organic **solvents** must be flashed off before the **UV/EB** cure, and generally increase **VOC** emissions that may need to be controlled by add-on emission control technology. Water can successfully lower viscosity of some **UV/EB**-cured **coatings** without introducing **VOC**.⁴⁰ However, when either an organic **solvent** or water is used to adjust viscosity, additional drying time, space and energy is required.

The same paint spray booth used to apply conventional **coatings** can be used for **UV/EB** applications. A paint spray booth where conventional **coatings** are applied must have positive air flow through it to avoid accumulation of combustible or explosive vapors, and to carry **VOC** and **overspray** away from workers. Because **UV/EB** paints contain little or no **VOC** (unless **VOC** is used to adjust viscosity), **overspray** is the primary concern in **UV/EB** applications. As a result, if **VOC** is not present, less airflow may be needed. **Overspray** in a **UV/EB** application is carried to an **overspray** arrester (a kind of air filter) to protect workers. **Overspray** collected from an arrester can be reused because **UV/EB coatings** retain their fluidity and do not dry out. However, if **solvent** was added to adjust viscosity, addition of **solvent** may be required before reuse of captured **overspray**.

Transfer efficiency for a particular spray application technique is about the same for both conventional and **UV/EB coatings**. However, collection and reuse of **UV/EB overspray** can improve the overall effectiveness of a **coating** operation; that is, the ratio of **coating** solids applied on a **substrate** to the total amount of **coating** solids consumed improves because reusing the **UV/EB coating overspray** reduces overall **coating** consumption. For example, when **transfer efficiency** is about 50%, the overall effectiveness of a **coating** operation may improve to about 95% with **UV/EB coatings** by using an arrester that captures 90% of the **overspray** and reuse of that **overspray**. Similarly, electrostatic spray guns normally have a 90% **transfer efficiency**, but the overall effectiveness of a **coating** operation using electrostatic spray guns can be about 99% for **UV/EB coatings** when the **Overspray** is captured and reused.

Other Application Techniques

High speed spinners are used to apply **UV/EB coatings** in microelectronics. A photoresist **coating** is applied to the center of a **substrate**, that is then spun to leave only a thin coat on the **substrate**. The **UV/EB photoresist coating** may contain a **solvent** or be heated to reduce viscosity, if necessary to control **coating** thickness. (Note: Conventional photoresist contains a **solvent** that must evaporate to allow this thin film.) The **UV/EB coating** is then cured in selected areas by exposure to radiant energy. The uncured areas are then washed away by **solvent** to expose uncured areas to etching, doping to change the electronic properties, oxidation to form insulators, or deposition of metal to form conductors. The **coating** is then stripped off and another **coating** applied for the next step in the process.

Flow or curtain **coating** is used with objects that move through a flowing curtain of **coating** (similar to a waterfall). This technique is used to advantage with **UV/EB coatings** because they lack volatile ingredients. Volatile ingredients in conventional **coatings** would require replacement to compensate for evaporation from the flowing curtain.

PART II: THE DETAILS

Now that you have a basic understanding of **UV/EB coatings, inks and adhesives** and how they differ from conventional **solvent** borne and waterborne systems, you probably have some insightful questions. In this section we attempt to answer those questions and provide details on **UV/EB** technology and its application.

UV/EB RADIANT ENERGY

In this section **UV/EB radiant energy** is discussed in detail. Topics cover **UV/EB radiant energy** sources, **UV/EB ionizing radiation** and **UV/EB radiation** penetration. As previously noted, there has been a lot of confusion about the term **radiation** and we have tried to use the term **UV/EB radiant energy** to avoid this confusion. However, as we discuss certain topics the term **radiation** will be used. As you read these sections, keep in mind that **UV/EB radiation** and **radioactivity** are not the same, and should not be confused. The only connection between **UV/EB radiation** and **radioactivity** is purely linguistic (i.e., both **radiation** and **radioactivity** use the root radi- to describe radial propagation of energy by particles and **electromagnetic waves** from a source). Refer to Appendix A, Ultraviolet and Electron Beam Radiation vs. Radioactivity, for additional information.

UV radiant energy does not penetrate the skin, but can cause sunburn and tanning of the top layer of skin - just like sunlight. **UV radiation** from curing units can be much more intense than that from sunlight and can burn or tan the skin quicker. When **UV** sources are properly shielded, eye irritation, skin tanning and sunburn do not occur. **EB** produces **x-rays** as high velocity electrons change speed and are absorbed by air, an **EB coating, ink, or adhesive**, the **substrate**, or an absorbing part of a printing press or **coating** apparatus. **X-rays** can and do penetrate human tissue, but proper shielding of **EB**-curing units reduces this hazard to below background levels.

HOW IS UV/EB RADIANT ENERGY GENERATED?

Sources of **UV** and **EB radiant energy** are quite different. Therefore, each will be discussed independently. In general, **UV radiant energy** sources have evolved for continuous and discrete flat (2 dimensional) and **3D** production, but **EB** has remained largely a continuous flat process with only a few instances of use for discrete **3D** production.

UV Sources

UV radiant energy is often generated by electric arcs in medium-pressure (about two atmospheres) mercury vapor arc lamps, as shown in Figure 2. These lamps are generally made of quartz formed into a long cylindrical tube to provide uniform illumination over the width of

the **web**. The lamps also contain a gas, such as argon, that aids in ionizing mercury. When a startup arc is operating, the mercury in the lamp has not yet fully vaporized and, for several minutes, both the spectrum and intensity of **radiation** are changing. In addition, mercury vapor arc bulbs have a very nonlinear current versus voltage characteristic. As a result, they require a ballast - similar to fluorescent lamps, but at higher power. Various designs of these ballasts have had their performance evaluated. There is truly no single answer for all applications, but ballast selection is based on a tradeoff of cost, size, noise, and power.⁴² The length of the cylindrical quartz tube with electrodes limits the width of the **web** that can be used. For mercury arc lamps, this has a practical limit of about 5 feet.

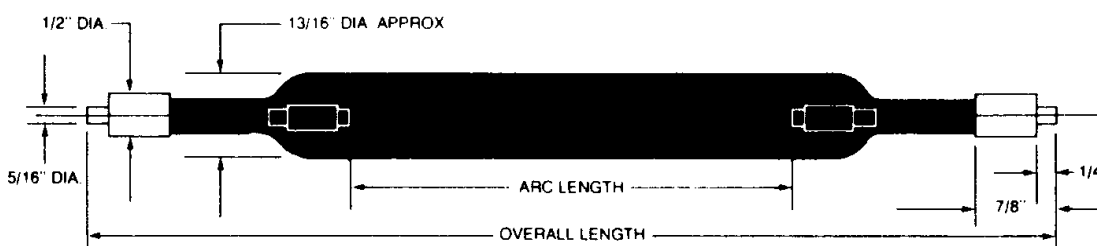


Figure 2: UV Mercury Arc Lamp

Microwave excited bulbs, another source of **UV radiation**, are filled with mercury vapor and an easily ionized starter gas such as argon or xenon (See Figure 3). Light is produced by a plasma which is generated by microwave **radiation** and, as a result, these bulbs do not have electrodes penetrating the quartz envelope. Because these electrodes are absent, microwave excited lamps are not subject to leakage or breakage around such electrodes. Consequently, microwave excited lamps tend to last much longer than arc lamps. Because space is not required for electrodes, microwave excited bulbs can achieve cures on very wide **webs** (up to six meters or 20 feet) and conceivably more. Microwave excited lamps can be shaped to give more uniform **3D** curing and are not constrained to a long cylindrical geometry. Therefore, they can assume any shape that the optical designers have in mind and that lamp manufacturers can make. Microwave excited lamps may be used intermittently because they start up nearly immediately. They also can be operated continuously.

Recently, lamps have been developed which operate without elevated temperatures, are instant-on, and produce a line spectrum in the **near-UV** which does not generate ozone.³²

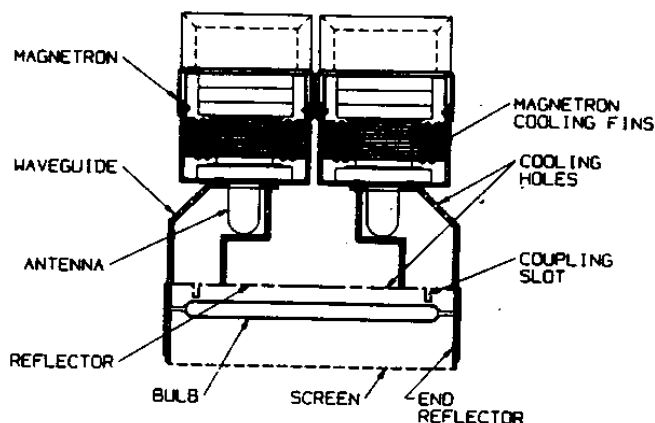


Figure 3: Microwave Excited Bulb with Generator

There are also xenon or argon arc lamps which use **excimers** to generate **UV**. These generate a thermal plasma in xenon or argon gas which then excites an **excimer**. It appears that pulsed high intensity radiance from these lamps can penetrate even better than a steady lower intensity radiance from mercury vapor lamps. These arc lamps can be pulsed repetitively (strobed) to give essentially continuous curing, or can be used for **UV radiation** which is required only intermittently at a point (such as with hand-held sources). The rate and number of flashes can be adjusted to give a required dose for curing. Hand-held **UV** point sources use much less power, use a mirror to focus energy, and can use a wand or optical fiber to direct energy. Hand held sources are used to splice optical fibers, bond lenses, bond items to printed circuit boards, encapsulate small electronic components, or even bond artwork. These compact hand-held sources produce less heat and consume less power with greater **UV** penetration than either mercury arc lamps or microwave excited mercury vapor lamps.

Addition of **excimers** to mercury vapor arc lamps, microwave excited lamps, or argon or xenon filed arc lamps can generate more radiant output in selected **near-UV** or actinic portions of the spectrum. For example, a Fusion **UV** Systems “D” filled bulb has an **excimer** that can produce a broad spectrum with peak intensity at 370-380 nm. **Excimers** are excited dimers. These molecules get excited, separate, and recombine while releasing energy in a given and sometimes narrow band of wavelengths. **Excimers** can emit shorter wavelengths than that of **photons** used to excite them. This happens because more than one **photon** can excite a **dimer** molecule to cause it to separate, but only one **photon** is emitted when the molecule recombines. The **excimer** is not consumed in this process. By comparison, the phenomenon of **fluorescence** always produces longer wavelengths than that of an absorbed **photon**. **Fluorescence** is caused by a molecule absorbing a **photon** and reradiating the energy at a defined longer wavelength.

Whenever mercury vapor or **excimers** are used, bulbs that have reached their end of life should be disposed of properly. This may require crushing lamps to recover mercury, recycling of quartz, capture of any **excimers** that may be hazardous pollutants, and recovery of electrodes.

A lamp is often backed by a semi-elliptical mirror to focus **radiation** and obtain the highest intensity (See Figure 4). An ellipse has two foci. By placing a source at one focus, the image of that source appears at the other focus. The reflected **UV radiation** is focused to achieve as much intensity as possible because both wavelength and intensity play a role in curing. Intensity is the energy flow or rate at which **photons** are being absorbed. More than one **photon** can be absorbed by a molecule and the absorbed **photon** energies are available for ionization. This allows other longer (del) wavelengths to play a part in curing too.

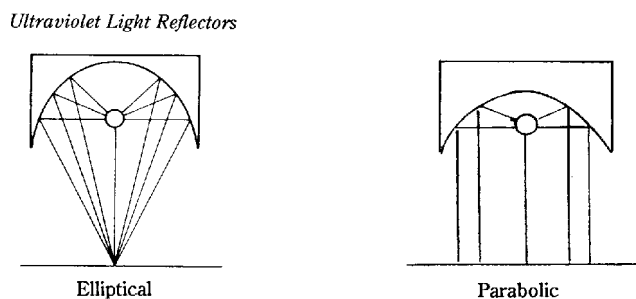


Figure 4: UV Light Reflectors

Lamps also can be backed by parabolic reflectors. As shown in Figure 4, parabolic reflectors have only one focus that sends light from the focus as parallel rays away from the reflector. A wide variety of dimpled reflectors and diffusing surfaces also are used where a sharp focus and high intensity are not needed. All types of reflectors are used, but for different types of cures.

More than one **UV** lamp may be required in a **UV**-curing unit. The dose that objects (e.g., **web** in printing, or furniture in a **3D** cure) receive from **UV** lamps is determined by the power of the lamps, intensity of **radiation**, absorption of **radiation** through an **ink, coating, or adhesive**, absorption of the **UV radiant energy** spectrum by the **photoinitiator**, and the speed that objects flow through **UV radiant energy** in a curing unit. In printing and **web coating, web** speed (rate at which a **substrate** passes through a curing unit) determines production rate. Production rates with **UV**-curing have been increasing as lamps become more efficient and powerful and as advances in **UV**-cured material chemistry have enhanced **polymerization**.

The **UV radiant energy** source must be selected to match the absorption requirements of the **photoinitiator** that the lamps are to activate. The source must also provide **UV radiant energy** over the entire surface of the applied film, given the configuration of the product. Therefore, the intensity of **UV radiant energy** must penetrate well enough to cure a **UV ink, coating or adhesive** all the way through; the **UV** material must cure with the chosen **photoinitiator**; and, the **UV radiant energy** source must be compatible with the **photoinitiator** and the shape of the **substrate**. For all **UV** lamps, a large portion of their spectrum (See Figure 5) fails to match the absorption of either the **UV**-cured material or the **photoinitiator** that is being used. Lamps and **excimers** are selected on the basis that their output peaks at the wavelength of maximum absorption of the **photoinitiator**. Lamps and **excimers** should be selected on the basis of their

output of an emitted energy intensity peak that the **photoinitiator** absorbs, because the **photoinitiator** is used to gain sensitivity and minimize the **UV radiant energy** dose required for curing. When energy consumption must be addressed, the **photoinitiator** must be a concern.

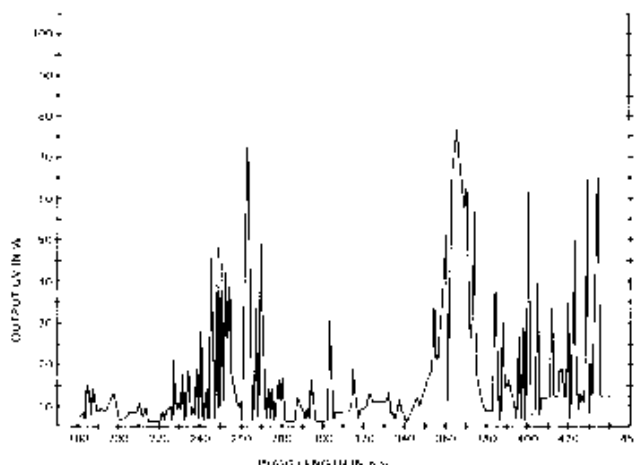


Figure 5: Spectrum of **UV** From a Mercury Vapor Lamp (having no excimer)

UV is generally transmitted a short distance (up to 25-50 cm or 10-20 inches) through air or a nitrogen atmosphere to minimize ozone formation. Because air and nitrogen are essentially transparent to **UV**, and aerosol particles that would cause **UV** scattering are sparse, this distance is not critical. Direct ozone and NO_2 generation is not a problem if an oxygen-free **nitrogen blanket**, an ozone-free lamp, or a quartz filter is used. Ozone-free mercury bulbs are made of a type of quartz that strongly absorbs energy below 260 nm in wavelength.

Mercury vapor arc lamps can take several minutes to warm up. A shutter is usually provided to protect the **web** and prevent fires during warm up. If there is no shutter, a printing or **coating** line is kept running to prevent the **web** from melting or catching fire while the lamps warm up. A **substrate** or **web** that passes through a press or coater during bulb warmup becomes solid waste with uncured **UV ink** or **coating** on it. This can be hazardous solid waste because the **UV ink** and/or **coating** is not cured. It can be converted to solid non-hazardous waste simply by exposing it to enough sunlight. A shutter that remains closed also can protect a stationary **web** until mercury vapor arc lamps are warmed up and minimizes such waste.

Both mercury vapor arc lamps and microwave excited lamps normally operate at about 800°C . **IR radiant energy** from each is proportional to their surface areas. Mercury vapor arc lamps have over twice the surface area for the same **UV** radiance and, therefore, over twice the **IR radiant energy** compared to microwave excited lamps. As a result, mercury vapor arc lamps will cause a greater temperature rise in a **substrate** for the same **UV** dose.

To prevent **web** damage from heat (highly focused **IR radiant energy**) and a fire hazard when a **web** breaks or stops, **UV**-curing devices are usually equipped with one of the following: (1) deionized water in tubes to absorb **IR radiant energy**; (2) a dichroic optical system (See Figure 6) (3) a shutter that automatically closes when the **web** stops; or (4) a cold light source. In option (1), flowing de-ionized water transmits **UV** while absorbing the **IR**. A dichroic optical system (2) uses **coatings** on the reflector that transmit **UV** with much lower interference losses than they do for **IR radiant energy** and, therefore, reduce incidental **IR** reaching the **web**. A properly ventilated shutter (3) absorbs all **radiation** while the **web** is moving too slowly. In option (4), the light source lacks any **IR** that would ignite a **web**.

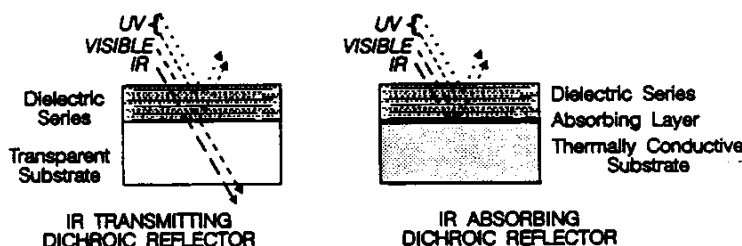


Figure 6: Dichroic Coatings

EB Sources

Electron guns are used to generate **electron beams** in a manner similar to a TV picture tube. These beams can be deflected, just like a beam that forms a raster on a TV screen or computer monitor. A beam from these electron guns can be focused magnetically to create a small spot that moves rapidly. **Electron beams** also may be generated by linear filaments and cathodes that are then directed by electrostatic electrodes to form their image on a **substrate**, as in Figure 7. Multiple filaments or cathodes can be used when higher currents for higher production speeds are required.

An **EB** is capable of curing printing **ink** within a very short length of curing unit (excluding those parts required for shielding and baffles), and has sufficient curing capability to allow high **web** speeds. Older **EB**-curing units often had more production capacity than was needed. Because of the cost of shielding and handling high voltages, as well as improvements in **EB inks, coatings, adhesives** and **photoinitiators**, there has been a trend to produce smaller electron guns with lower voltages. Although **Photoinitiators** are frequently not needed for **EB** cures, they have been used to cure thick films on **three-dimensional** objects with a lower **EB** voltage.

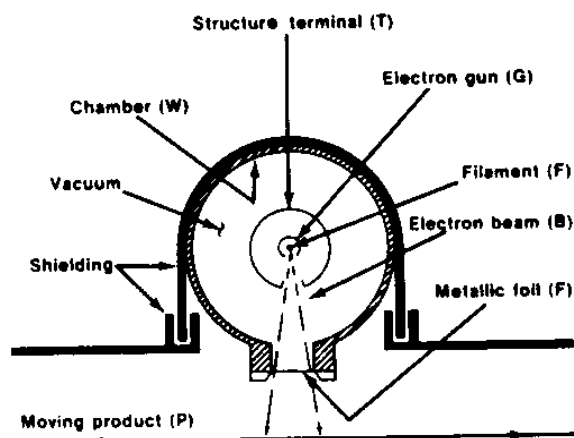


Figure 7: Schematic of Electron Gun

Early **EB**-curing units used with (and usually attached to) printing presses were relatively large compared to **UV**-curing units because, **EB** units had to include much more shielding (some even used concrete vaults to enclose a press). These early **EB** units had much greater production (curing) capacity than early **UV** units and used up to 10 MV to accelerate electrons. Current state-of-the-art electron guns use about 35 kV in a package about 3 inches in diameter by 12 inches long. As a result of this substantial reduction in energy, current **EB**-curing units do not require as massive a shield. Excess production capacity associated with **EB** in past years is becoming smaller, and production capacity for both **UV** and **EB** is converging to a point originally between the two techniques. In addition, greater efficiency in **EB** power use is obtained by using **cationic photoinitiators** and has resulted in lower voltage sources.

Electron beams are sensitive to the density of the gas between an **EB** source and an object to be cured. An **EB** will ionize oxygen in air to create ozone and nitrogen oxide; therefore, a **nitrogen blanket** is highly recommended to avoid nitrogen oxide and ozone formation.

Electrons are slowed down by multiple impacts with gas molecules surrounding a **substrate** (presumably nitrogen, but the same is true of oxygen). This causes an **electron beam** to degenerate into a diffuse multiple scattering of electrons. Scattered electrons are much more numerous than electrons in the original beam, because they result from an avalanche effect. Scattering occurs because nuclei are surrounded by numerous electrons that have the same mass as electrons in the beam. To minimize this problem, a sealed evacuated space is provided from the **EB** source to within a small distance from the **substrate**. A titanium foil window forms the air-tight seal to maintain a vacuum for the evacuated space.

Titanium is chosen for the window because: (1) it has a low **atomic number (Z)** and is a low density metal that heats up by absorbing about half of the electrons in the beam, but does not heat up enough to lose its strength; (2) it can be made as a foil that is thin enough to minimize

losses of electrons; (3) it is strong enough to allow a thin foil to hold against atmospheric pressure, even when an **electron beam** is on; and (4) it is very corrosion resistant so it will not readily oxidize when moderately heated. Until titanium foil could be made (circa.1970), there was no suitable window material and, therefore, no energetic **electron beam** in air was possible. The electrons are directed at the foil window because they would lose too much energy going through a thicker metal wall. They would even lose too much energy by going through enough glass to provide an adequate seal for a vacuum.

When the electrons stream through the window, they encounter their first air or nitrogen molecules and are scattered rather strongly. Nevertheless, an intact stream of electrons continues for several millimeters (depending upon the initial velocity). This intact electron stream becomes more and more diffuse as the distance becomes greater. After only a few centimeters, the electron stream is scattered and diffuse. As the **electron beam** loses energy by impacts and capture, it generates **x-rays**. Finally only ions remain, with **x-rays** radiating from where the **electron beam** had been.

Electron beams are sensitive to the density of the gas surrounding the object to be cured and to ionizing oxygen in air (oxygen ions create ozone). After passing through a foil window, electrons are slowed down and scattered by impacts with molecular gases in air. As a result, a foil window must be placed very near (~ 1 mm) to a material that is to be cured at atmospheric pressure.

Vacuum chambers have been built to **EB**-cure filament reinforced plastic objects.¹⁸ These vacuum chambers are suitable for curing fiber reinforced composite objects that are small enough to fit within a chamber. These chambers are also suitable for **EB**-curing of **coatings** on the exterior of such objects. These chambers are not well-suited to continuous **coating** applications as in either rotogravure printing or **coating** optical fibers.

WHAT IS UV/EB IONIZING RADIATION?

Ionizing radiation is **radiation** that can ionize a molecule. Because all molecules are not ionized by the same amount of energy, the question becomes what molecule? The term **ionizing radiation** usually refers to the amount of **radiation** that will ionize oxygen in air; that is, **radiation** with a wavelength shorter than 253 nm (this includes **actinic UV radiant energy** generated in **UV**-curing systems and electrons and **x-rays** generated in **EB**-curing systems). **UV/EB-cured inks, coatings and adhesives** also contain other molecules that can be ionized by **radiation** at these wavelengths.

UV energy is selective in the molecules that it can ionize. On the other hand, **EB** energy ionizes anything in its path until all electrons are absorbed. **EB** systems generate **x-rays** when the electrons are absorbed. These **x-rays** also can ionize molecules.

Ionizing radiation can even mean visible light if a **photoinitiator** that is sensitive to a visible wavelength is used to ionize molecules. Even **IR** energy can ionize when it is intense enough to set an object on fire.

Both **UV** and **EB radiation** have **photons** or particles that are energetic enough to break molecular bonds. It is important to realize that **photons** of a given wavelength (or color if they are visible) are all at the same energy level and that energy level increases as the radiated wavelength gets smaller. The amount of energy in each **photon** is determined by the following formula:

$$\text{energy} = hf = hc/\lambda$$

where h = Planck's Constant

f = frequency

c = speed of light

λ = wavelength

Intensity indicates the number of **photons** striking a detector per unit of time. **Photons** have wavelength-defined energy until they are absorbed. Contrast this with the concept in quantum physics that views **photons** as massless particles that are used as an alternative to wave behavior. Describing the phenomenon as both a wave and a particle is not logical. How can a particle be everywhere a wave goes? How can a photon have only one energy, while a particle's energy varies. Yet both are used to describe the wave and particle characteristics of **radiation**. Knowing that this is the case, we now must deal with **ionizing radiation** that is used for **UV/EB-curing**.

OSHA does not include **UV** in its definition of **ionizing radiation**, although **UV** can ionize oxygen in air when the wavelength is below 253 nm. From an EPA viewpoint, **ionizing radiation** can be any wavelength shorter than blue light; therefore, **ionizing radiation** is any wavelength shorter than 400 nm. It can be **near-UV radiation** (315 - 400 nm wavelength), actinic or **far-UV radiation** (180 - 315 nm wavelength),¹ **x-rays** (0.1- 40 nm wavelength), or gamma rays (<0.1 nm wavelength).

Some sources define **ionizing radiation** having wavelengths between 40 nm and 180 nm as **UV**. However, the ozone generation capability of **electromagnetic waves** with wavelengths under 253 nm and the difficulty in generating these waves greatly restricts use of these wavelengths for curing **UV/EB** materials.

Another definition of **ionizing radiation** splits the **UV** spectrum into parts. It defines **UV-A** as 315-400nm, **UV-B** as 280-315 nm, **UV-C** as 200-280 nm, and Vacuum **UV** as 100-200 nm. In this scheme, **UV-A** is the lower wavelength limit for human vision, is transmitted by window glass, and can increase pigmentation of tissues. **UV-B** is primarily erythrogenic energy; that is, it will cause reddening of skin, increase pigmentation of tissue, and cause eye irritation. The most common effect of **UV-B** exposure is erythema (sunburn) that generally appears within three hours and becomes most severe about twelve hours after exposure. **UV-C** is filtered from

sunlight by ozone but, when man-made, has important sterilizing properties and other industrial uses. Use of **UV-C** or **Vacuum UV** requires an oxygen-free atmosphere to prevent formation of ozone.

Some materials need more energy to ionize than that supplied by a collision with one **photon** of available **radiation** in a brief period of time and are, therefore, dependent on the intensity of **radiation** for ionization. Intensity is the rate at which **photons** are absorbed. Even long wavelength **IR radiation** can ionize molecules if it is sufficiently intense. However, **IR radiation** is not usually considered **ionizing radiation** for curing because it either melts or burns **substrates**. Only **photons** of shorter wavelengths and electrons actually have enough energy to cause ionization of **UV/EB-cured ink, coating and adhesive** molecules to happen without damaging a **substrate**.

The intensity of **UV** is measured in Watts per square centimeter. Doses of **x-rays** and gamma rays are measured in either **Roentgens** (1Roentgen; R = 100 ergs/gram) or the **Roentgen Equivalent for Mankind (REM**, which is the integral over the whole spectrum of **Roentgens** times the adsorption factor for human tissue).² The dose of **electron beams** is measured in **Gray** absorbed **radiation** units (1.0 Gy = 1.0 Joule/kg).

HOW DEEPLY DOES IONIZING RADIATION PENETRATE?

UV Ionizing Radiation

UV radiant energy penetrates to only a shallow depth in a **coating, ink or adhesive**, clothing, or human skin. Therefore, **UV radiant energy** is usually used for thin film applications such as printing **ink**, pressure sensitive **adhesives**, permanent **adhesive** assembly, or some paints. **UV radiant energy** is absorbed by pigments, **monomers, oligomers** and **photoinitiator** sensitive to that **UV** wavelength to break molecular bonds. Air or nitrogen is essentially transparent to **UV**. However, an **ink, coating or adhesive** will deplete **UV radiant energy** within a shallow depth, often less than a thousandth of an inch.

EB Ionizing Radiation

In **EB-curing**, electrons have a limited range before scattering in air. They also have a limited range (1 - 20 mm) within the material to be cured. This range is a function of the speed of the electrons (usually measured in electron volts) at the surface of the material being cured, the density of that material, and the **atomic number (Z)** of the molecules that make up the material. As **EB** voltage increases electrons move faster and, as electrons move faster, they penetrate more deeply. For electrons and **x-rays**, higher **Z** materials have greater absorption potential because an **EB** is attenuated by reacting with orbital electrons. Most nuclei in **EB-cured** materials have about the same low capture cross-section for scattered electrons as they do for high energy

electrons. An **EB** ionizes (changes the electronic balance of) atoms and molecules that capture it. Electrons in a beam lose energy to electrons that they impact and slow down. Electrons are captured more readily (i.e., the capture cross-section is greater) when they are moving slower.

These fast moving electrons in a beam are retarded by impacts with the orbiting electrons of atoms and the positive charge on the nuclei. This happens with air molecules as well as molecules in the **EB**-cured material. Electrons that are impacted may either gain escape velocity or go into larger orbits. Electrons that gain escape velocity are referred to as being scattered. Scattered electrons, and those that go into larger orbits, cause the atom to radiate energy as **x-rays**. Scattered electrons impact other atoms and produce an avalanche of lower energy electrons that replace electrons that were lost.

As electrons in a beam slow down, they generate **x-rays**. These **x-rays** are called *brehmsstrahlung*, which is a German word meaning “braking **radiation**” or “**radiation** caused by retardation.” This results from the slowing of electrons, scattering of electrons, acceleration of orbiting electrons, and cyclotron **radiation** are caused by larger electron orbits. Cyclotron **radiation** produces a characteristic narrow band **x-ray** spectrum emission of *brehmsstrahlung* at wavelengths that depend upon the particular capturing atoms. Low **Z** materials generate longer wavelength **x-rays** that do not penetrate as much. Collisions with high **Z** materials tend to produce more energetic **x-rays** that can penetrate more readily. Electrons that escape orbit produce a broad spectrum of **x-rays**. All man-made **x-rays** are generated in this way.

The extent to which **x-rays** from **EB radiation** penetrate is related to the **Z** of the material, and the density that is penetrated. **X-rays** generally penetrate lower **Z** materials to a greater depth. Higher material density places more atomic cross-sections along the trajectory, which causes a greater attenuation. Attenuation is the term that is used to describe the amount that **x-rays** are absorbed. **X-rays** resulting from older **EB** systems with significant excess capacity have required a concrete vault or other appropriate shielding around the printing press to contain and attenuate them.

Most **substrates** and **EB**-cured materials are composed of oxygen, hydrogen, carbon, and nitrogen atoms. These are all low **Z** materials. Some pigments and additives contain high **Z** materials, but the effect of these is mitigated by a thin film of material. Therefore, penetration of low energy **x-rays** through the **EB**-cured materials and **substrates** is usually very great. When higher **Z** atoms are excited by **EB**, a higher penetration **x-ray** is generated. These **x-ray** generated **photons** also can ionize molecules in **EB**-cured materials, just as an **electron beam** and **UV radiant energy** do more directly.

Because an **EB** will be absorbed and **x-rays** will be generated, **x-rays** will have to be attenuated. This is now done by insertion of dense heavy metal shields in a curing unit. It also can be done by enclosing a press within a concrete vault. The walls of such a vault might be made thinner by addition of insoluble heavy, metal salts as a filler.

UV/EB-CURING

In this section more details are provided on **UV/EB coating, ink and adhesive** formation, **photoinitiators**, the relationship between film (applied **coating, ink or adhesive**) thickness and production rate, **3D** capabilities, measuring the extent of curing, and anything else that you need to know about **UV/EB-curing**

HOW DO UV/EB COATINGS, INKS AND ADHESIVES FORM?

UV/EB materials cure (form a solid film) by **polymerization** and **crosslinking**. There are many **polymerization** mechanisms; however, currently only two **polymerization** mechanisms are used for **UV/EB-curing**: **free radical polymerization** and **cationic polymerization**. Except for powder **coatings**, most **UV/EB coatings** start out as a liquid. **UV/EB-cured powder coatings** start out as solid particles that are applied to a **substrate**, subjected to **infrared radiant energy** (heat) to melt them, and then exposed to **UV/EB radiant energy** to polymerize the **coating**. **UV/EB radiant energy** breaks the **photoinitiator** molecule in the **UV/EB** material by either homolytic fission (to make **free radicals**), or heterolytic fission (to make cations and anions). This fission refers to breaking a molecule rather than an atom. (It does not mean the same thing as the term used for nuclear reactions.) These **free radicals** and cations then combine with **monomer** or **oligomer** molecules to form a **polymer**.

The properties of a **polymer** are the result of: (1) **monomer** and **oligomer** molecules that have become part of the **polymer** chain; (2) **crosslinking** that is accomplished by pendant groups; and (3) the length of the **polymer** chain before termination. A **polymer** molecule can be terminated in one of three ways:

1. One chain bonds endwise to another, which creates a pair of electrons that will not react further, or
2. An oxygen atom reacts with the free electron in a **free radical** and creates a pair of electrons that will not react further, or
3. **Polymer** molecules limit the mobility of **monomer** molecules so that the reaction stops due to the unavailability of reactants, and the **free radical** reaches the end of its lifetime.

The second termination mechanism is also referred to as **oxygen inhibition**. Note that this is only an issue in **free radical polymerization**, not **cationic polymerization**. **Oxygen inhibition** is avoided by blanketing the reaction area with dry nitrogen to exclude oxygen that would otherwise be present in ambient air. The presence of oxygen molecules could cause **polymer** chains to be terminated too short, or limit **crosslinking**.

The types of **monomers** or **oligomers** define the structure of the **polymer** and, therefore, its properties. The basic properties are modified by **crosslinking** that molecularly bonds the

polymer chains together.

While we might like to think that a time integrated dose of **UV/EB radiant energy** causes a cure, intensity (the rate at which **photon** energy is absorbed) is also important. Molecules at the surface (the topmost level) may receive 100 or more times the intensity of **UV/EB** energy as molecules at the bottommost level adjacent to the **substrate**. As a result, adhesion failure may occur if bottommost **coating** molecules do not receive enough radiant energy to cure.

Free Radical Polymerization

A **free radical** is a molecular fragment that has a single free valence electron (See Figure 8). **Photoinitiators** are unsaturated molecules (having aromatic or aryl carbon rings) that form **free radicals** very readily. Valence electrons are unreactive when paired with another valence electron; however, a single valence electron always seeks a second valence electron. A free valence electron is formed by homolytic fission. This occurs when sufficient **UV/EB radiant energy** is absorbed by the **photoinitiator** molecule. Homolytic fission means that both fragments are **free radicals** with single electrons available. **Free radicals** exist for a limited time and must find and react with **monomers** and **oligomers** within their lifetime.

Free radical polymerization contains the following steps:

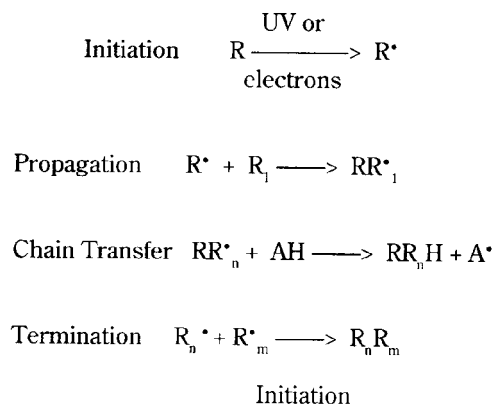


Figure 8: Free Radical Polymerization

When a **free radical** captures an electron from a **monomer** or **oligomer**, that **monomer** or **oligomer** becomes part of the **free radical**. A single valence electron is always left free after this joining and this new expanded **free radical** reacts again and again as it forms a **polymer**. This is a chain reaction. In this way, **monomers** and **oligomers** form **polymers** that contain long chains of **monomer** molecules.

Cationic Polymerization

Cationic photoinitiators are unsaturated molecules that break apart by heterolytic fission under **UV/EB radiant energy** to form cations and anions. Heterolytic fission means that the fragments are different. Cation fragments initiate and sustain the **polymerization** process, as in Figure 9. The anions do not contribute much to **polymerization**. The cations are either **Bronsted acids** or **Lewis acids**. These strong organic acids are positive ions that either donate protons or absorb electrons and are attracted to a cathode just as hydrogen ions are. The cations also cause fission to continue until all available **photoinitiator** molecules have ionized. Therefore, once started, **polymerization** will spread throughout the **UV/EB** material. Unlike **free radical polymerization**, **cationic polymerization** is an ionic reaction that cannot be terminated by a reaction with oxygen molecules. Because anions are also formed, the overall state of the **polymer** is neutral, even though **polymerization** occurs because cations are present.

Because **cationic photoinitiators** now exist, the list of potential applications that can be served changes and expands. These **cationic photoinitiators** can be used to polymerize **coatings** that, because of absorption, shadowing, or pigmentation, cannot receive enough radiant energy throughout their depth. Once **cationic polymerization** starts, it will continue to completion, even in the dark.

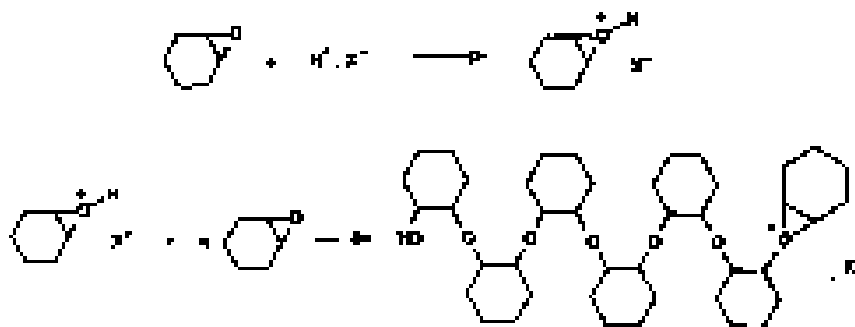


Figure 9: Cationic Polymerization

Crosslinking

Crosslinking can result from either **free radical polymerization** or **cationic polymerization**. It occurs as part of **polymerization** when pendant groups on one chain connect with pendant groups on another chain. **Crosslinking** produces mechanical hardness, resistance to melting, resistance to mechanical deformation, greater strength, and mar resistance (See Figure 10).

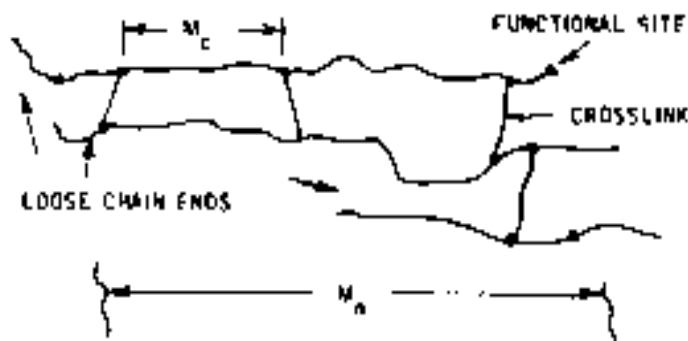


Figure 10: An Example of Crosslinking

HOW DO PHOTOINITIATORS WORK?

Photoinitiators are unsaturated, aromatic, aryl compounds that are more sensitive to **UV/EB radiant energy** than **monomers** and **oligomers**. Compared to **monomers** and **oligomers**, **photoinitiators** represent a small percentage of the weight of a **coating, ink** or **adhesive** that is being applied. Most absorption of **UV/EB radiant energy** in a **UV/EB-cured material** is accomplished by a **photoinitiator**.

Photoinitiator molecules fission (break apart) in predictable ways when they receive **UV/EB radiant energy**. They either form **free radicals** or cations as fragments. Therefore, **photoinitiators** play a critical role in initiating **free radical** or **cationic polymerization** in **UV/EB materials**. The type of **photoinitiator** must be selected with care. The energy absorption potential of a **photoinitiator** must be matched to the wavelength of peak radiant energy that is generated by the **UV/EB** source in order for the **photoinitiator** to do its job properly. If radiant energy is not sufficiently intense, a **photoinitiator** may not receive enough energy to form **free radicals** or cations. **Photoinitiators** also are major absorbers of **UV/EB radiant energy**.

DOES PRODUCTION RATE DEPEND ON COATING THICKNESS?

Coating thickness does affect production rate. Because the thickness of material applied by spray and roller methods (>0.001 inch) are typically much greater than that of printing ($<<0.001$ inch), they require a larger dose of **radiation** to cure. Therefore, for a constant radiant energy source, production rate must decrease as film thickness increases in order to provide adequate exposure to radiant energy needed to cure the material. In reality, the intensity is adjusted to cure the coating at the production rate.

This is exacerbated by absorption of radiant energy by the **UV** material itself, because the intensity of **UV radiant energy** will decrease severely with film thickness. This may be offset

with more intense **UV**. However, **IR radiant energy** (heat) is absorbed along with **UV** energy. Therefore, the limit in **UV** intensity is determined by the **IR** energy that is absorbed by the **substrate** and **coating**.

Thin material applications (as used in printing and **adhesive coating**) can cure almost immediately. Production rates for these applications can be much higher than for thicker applications. Printing production speeds of over 1,000 feet per minute can be achieved with complete curing in a **UV**-curing unit that is only a few feet long.

Cure times for thicker applications using spray or roller techniques may be measured in seconds. **3D** fiber reinforced composite structures contain fibers that shadow much of the **UV/EB coating** that bonds the fibers together. Curing a **coating** in this type of structure can require **EB radiant energy**, **cationic** curing, or both. Cure time may be greatly extended, though **3D** cures can be accomplished in seconds.

WHY HAS THERE BEEN GROWTH IN 3D CAPABILITIES?

As previously stated, **UV/EB**-cured materials were first used in printing processes because this technology is well suited to a thin **coating** of **ink** on a flat surface. **UV/EB** technology was also well suited to **coating** sheet metal before it was coiled and flat wood product panels for the same reasons. However, other applications arose, such as optical fibers, that were not flat. These **3D** applications have the ability to cast shadows that hide portions of the surface from the radiant energy needed to cure the **UV/EB** material. By **3D** capabilities we mean the ability to cure **coatings** on **3D** objects.

Figure 11 shows a cross-section of an optical fiber used for transmission of digital signals and the special **coatings** that are crucial to its performance. Without these **coatings**, fiber optics could not be a long-distance medium. The innermost **coating** must have a low index of refraction, and not absorb the wavelength of the laser that is being used to send the digital signals. The next **coating** must provide strength. The outermost **coating** must strongly absorb the wavelength that is being used to prevent “cross-talk” between fibers. The development and availability of these **UV/EB coatings** were crucial to the success of fiber optic cable, because no other technology could provide the rapid cure with 100% integrity. As a result, equipment and **UV/EB coating** developers and manufacturers cooperated to produce this product and the other products that use **UV/EB** materials.

Because efforts to minimize the effect of the shadow in **3D** applications succeeded in optical fiber manufacturing, the advancement of **3D** capabilities in other applications became only a matter of time. Currently the effects of shadows can be minimized for wood furniture and even automobile bodies. This has been achieved by multiple radiant energy sources, dimpled reflectors, and myriad other optical design techniques.

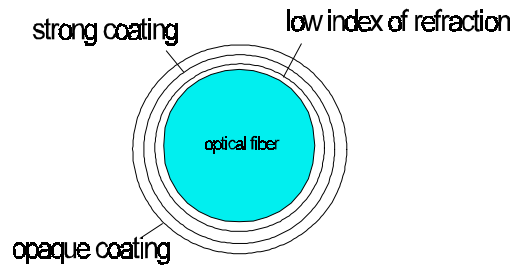


Figure 11: Schematic of Optical Fiber

Manufacturing plants now spray or roller coat **UV** sealers, primers, finish, and topcoats on panels and furniture and rapidly cure these materials within 25°C of room temperature. Conventional **coatings** on a wood **substrate** can not be heated enough to cure in less than an hour. Because the curing time is so short for **UV** materials, fine furniture manufactures use **UV coatings** to avoid dust blemishes. In addition, because there are no flammable **VOC** to cause a fire hazard, at least one insurance company has decreased the fire insurance premiums by 15% where **UV** material are used.

Use of a computer guided **UV** optical fiber or laser has allowed layer-by-layer construction of objects using a **polymer**. The **polymer** object that is formed can be either a model or the final part. This technique is referred to as stereo lithography. This is done by retreating a platform beneath the surface of a **monomer** or **oligomer** while a computer guided **UV** source operates like a printer tracing a raster with the **UV** source “on” over the solid portion, and “off” over open spaces or cavities in the structure of each successive cross-section. In this way, a scale model (any scale including life size) of a complex part can be made - even body parts can be generated from a CAT or MRI scan. This technique allows for troubleshooting of designs. It can even allow surgeons to practice on life-size models of the patient.

HOW IS EXTENT OF CURING MEASURED?

The extent of a **UV/EB coating** cure has been measured by adhesion, solvent-rub, stain tests, ion mobility, glass transition temperature, mechanical properties such as elastic modulus or tensile strength, Taber abrasion, a fluorescent indicator, or by minimum volatility. The measure is selected based on some performance measure that is germane to endurance, and no correlation has been made between the various cure measurement techniques. A few of the main tests are discussed here.

Adhesion of a **coating** is measured by the force per inch of edge that is peeled. When the **coating** is liquid, this force is near zero. It becomes a finite amount as curing progresses. When it approaches a maximum force, the slope of the peel force with increased **UV/EB** exposure approaches zero. Further exposure is said to overcure the material. Overcuring is thought to accomplish further **crosslinking** between molecules and react some additional **monomer**.

Taber abrasion tests the resistance to abrasion. It is based on the use of a weight (250 gram, 500 gram, or 1 kilogram) bearing down on an abrasive disk while the specimen is rotated against it. The abrasive disk can be any of a large number of types, based upon the purpose for which a **coating** is intended.

Solvent-rub is a modification of abrasion that requires a specified **solvent** to be present. This test measures the effect of the **solvent** on the cured **coating**. Presumably, an uncured or shallowly-cured **coating** would be readily removed by the **solvent**.

Ion mobility is measured by placing two electrodes on a **coating**, applying a voltage and measuring the current. Both the amount of current and the time response to switching the voltage on are measured. Both of these measurements provide diagnostics as to the ion mobility. Presumably, the ion mobility is least in an overcured **coating**. A minimum ion mobility that is acceptable to the usage is specified.

Elastic modulus is based on the slope of the stress-strain curve. This test requires a specimen to be coated for measurement of stress versus strain. Stress is the force per unit area to achieve the strain. Strain is the elongation per unit length that results. A higher elastic modulus requires more stress to achieve a given strain.

Tensile strength is the maximum stress that can be achieved before breaking. Typically, this occurs when a discontinuity in the stress versus strain curve occurs.

Minimum volatility is measured by weighing a specimen of cured **coating** to determine weight loss. Curing is done in increments with weight measurements at each increment. Between increments, temperature can be elevated to drive off volatile ingredients. A minimum volatility cure is the point at which weight loss reaches a minimum.

Glass transition is a property of the amorphous portion of a semi-crystalline solid. It is measured as the temperature at which the solid changes from a glassy deformation to a rubbery deformation. This is determined by measuring the elastic modulus at different temperatures, and finding the temperature interval in which the glass transition to a higher modulus occurs. A higher glass transition temperature (T_g) can be used as evidence of greater **crosslinking**. Alternatively, the minimum T_g can be specified and the elastic modulus is then determined at that temperature to determine whether it is glass-like or rubber-like.

The other methods are used less often because: they are more suited to research; are more expensive; or take too long to obtain a result while production is running. While each method ostensibly shows that curing is complete, the correlation of one method to another is seldom if

ever done. Whether food contact could or should be allowed is not determined by these tests (with the possible exception of ion mobility).

IS THERE ANYTHING ELSE THAT AFFECTS CURING?

You may have noticed that we have hardly mentioned temperature. **UV/EB** materials cure nearly instantaneously and cure even faster as temperature increases. Temperature is a measure of the kinetic energy of molecules. If the temperature gets above a critical level (a different level is critical for each **UV/EB** material) **polymerization** can occur in the absence of **UV/EB radiant energy**. The temperature of **UV/EB**-cured materials needs to be kept between 60°F and 80°F to preclude depletion of inhibitors in the material. This temperature range usually is not a problem, but air conditioning may be required in some cases.

Other factors are **UV** lamp variation during use, variations in power line voltage, oxidation effects and **infrared** effects. All of these vary with time and the effect of each may be different. Therefore, we should recognize that the cure will vary as a combined effect of all of these factors.

UV/EB materials can vary. To minimize variability, **UV/EB**-cured materials should not be exposed to peroxides, iron particles, or other **free radical** sources. In addition, they should be stored away from sunlight or other sources of radiant energy that could cause **polymerization**.

If a **UV/EB**-curing unit promoting **free radical polymerization** is exposed to atmospheric oxygen or atmospheric oxygen invades a “**nitrogen blanket**” used in the process, **oxygen inhibition** will occur. Oxygen can inhibit the curing of acrylics, polyesters, and styrenes. The effects of **oxygen inhibition** may result in the use of a far greater dose of radiant energy than expected to obtain a cure. This would be especially true if the “**nitrogen blanket**” were not used. On a positive note, **oxygen inhibition** is intentionally used to retain tack in some pressure sensitive **adhesives**.

Humidity can affect the curing time of **UV/EB** materials that use **cationic photoinitiators**. This effect differs for various **coatings**, **coating** thicknesses, **coating** permeabilities and water vapor concentrations.³⁸ In some cases, water can inhibit **polymerization** similar to **oxygen inhibition**. This can be corrected by using an **IR** dryer or an extended dry **nitrogen blanket**.

Monomers, oligomers, photoinitiators, fibers, and pigments in a **coating, ink** or **adhesive** can all absorb **UV/EB radiant energy**. The extent to which all of these materials absorb radiant energy can inhibit curing of the material, especially in thicker applications. Fibers and pigments can cast **UV/EB** shadows that prevent radiant energy from reaching **monomers, oligomers**, and **photoinitiators**. Materials that contain **cationic photoinitiators** do not have this problem. Material containing **cationic photoinitiators** only have to receive enough radiant energy to decompose the **photoinitiator** in the top layer and curing will be spontaneous after that.

PART III: EMISSIONS, HEALTH AND SAFETY

WHAT AIR POLLUTANTS ARE EMITTED FROM UV/EB-CURED MATERIALS?

UV/EB-curing is a very low emitter of air pollutants, but some emission do occur. This section discusses potential emissions of **VOC**, fine particulate, **HAP**, odors, ozone and NO_2 .

VOC Emissions:

UV/EB-cured **coatings, inks and adhesives** have a reputation for being **VOC**-free, but they actually do emit some cure volatiles that may be **VOC**. Although **VOC** emissions are extremely low from many applications using modern **UV/EB** materials (i.e., **VOC** emissions can be less than 1% of the weight of the **coating, ink** or **adhesive** used), cure volatile emissions for a typical application usually are in the 1-5% range. (Note that no **solvent diluent** is used in the typical case.) However, for a small number of applications, cure volatile emissions can approach 10% of the applied film weight. Even at the 10% level, uncontrolled **VOC** emissions are no worse than that of a conventional **coating** or printing operation equipped with good emission capture and control technology. Typically, no add-on control technology is either needed or used with **UV/EB**-cured materials.

UV/EB-cured materials are ready to use as provided by the manufacturer. No additives or blending is required after the **UV/EB**-cured materials leave the manufacturer. The one exception may be adding a **solvent** (**VOC** or water) to adjust viscosity in some spray or special applications. **UV/EB**-cured materials will not dry up unless subjected to sufficient **UV/EB radiant energy**. If **diluents** are present, uncured **UV/EB coatings** may simply become more viscous as the **diluent** evaporates. However, normally **VOC diluents** are not present.

Acrylates have been measured at a concentration of approximately 10 ppm in the space immediately above a **coating** (a headspace measurement) during cure. Concentrations of **VOC** in the same space were even lower.²⁸ Concentrations in a subsequent emission stream would tend to be even lower as a result of mixing and dilution with air in the exhaust stream. Such small emission concentrations are the desired goal of add-on emission control technology used with conventional processes, but they can be achieved by using **UV/EB-cured coatings, inks and adhesives** without a add-on emission control device.

EXAMPLE: Calculation of VOC Emissions

Source type: Printing

Application: Overcoating a 5 foot **Web** running at 1000 feet/minute

Coating characteristics: 0.8% specific gravity

Film thickness: 100 microns

VOC emissions: 1% of the film weight as applied

In this example, the source would produce 0.000163 pounds of **VOC** per square foot, or about 1.0 pound of **VOC** per 6,124 square feet. One pound of **VOC** would be emitted from overcoating 100% of a 5 foot **web** for 1.2 minutes at 1,000 feet/minute. This would provide a maximum of 72 pounds of **VOC** per hour, 576 pounds per 8 hour shift, or 52 tons per year per shift. In most cases **UV/EB** technology would qualify as a Lowest Achieved Emission Rate (LAER) technology. (LAER is required by the Clean Air Act on new and modified major sources locating in areas that are not attaining National Ambient Air Quality Standards.) In comparison, a conventional overcoating operation using **VOC solvent** would emit 2,600 - 3,600 tons per year of **VOC** for the same level of operation.

Note that the previous calculation was based on the amount of material that actually is applied to the **substrate**. In reality, some losses due to misting, spills, splatter, **transfer efficiency**, etc. may occur. Therefore, it would be preferable to use the mass of the total amount of **UV/EB**-cured material (**coating**, **ink**, etc.) that is consumed when calculating potential emissions from **UV/EB** printing and/or **coating** processes.

Fine Particulate Emissions:

When **UV/EB** materials are used on high speed printing presses and roll coaters, they will emit some mist. Mist is generated when **UV/EB** material that is between rollers and **substrate** rapidly separates in high speed applications. (Conventional materials also would mist if they were applied at as high a speed.) Misting of **UV/EB ink** in high speed printing has been measured at between 1% and 50% of the **ink** consumed. Many of the droplets were found to be under 2.5 μm (PM-2.5). Where misting is severe, users and suppliers can work together to minimize the problem.

HAP Emissions:

Unless **HAP solvents** are added, **UV/EB coatings** are **HAP**-free (i.e., do not contain any a **HAP** listed in Appendix E). However, fine droplets in mist generated by high speed rollers (see above) may contain toxic chemical compounds. You should check Material Safety Data Sheets (MSDS), review the **HAP** list, and/or contact the supplier to determine to what extent toxicity is an issue with a particular **UV/EB**-cured material.

Odorous Emissions:

Overall, the **UV/EB**-cured material used today have much less of an odor problem than material used 10 years ago. In fact, restaurant menus, packages for fine perfumes and boxes for chocolates can now be printed and coated with **UV/EB** (See Figure 12). However, **UV/EB** materials have historically emitted some objectionable odor, some even after curing. Odor generating **UV/EB** materials containing amines or sulfur compounds should be avoided where odor is an issue.

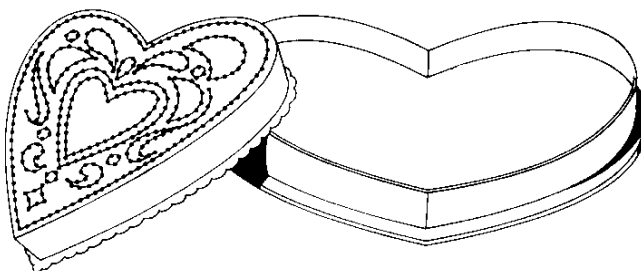


Figure 12: UV Coatings -- Now Used for Packaging Chocolates

Ozone and NO₂ Emissions:

Each form of **ionizing radiation** can ionize oxygen and generate ozone. Also, there is suspicion that NO₂ can be generated, too. However, total emission of ozone and NO₂ are relatively small and should not significantly affect concentrations of these pollutants in the atmosphere. Equipment manufacturers have reduced the potential for ozone and NO₂ generation from processes that use **UV/EB radiant energy**. **Nitrogen blankets** exclude air from the **polymerization** areas and, therefore, exclude oxygen as a reactant in these areas. However, air ventilation is used to remove heat from **UV** lamps; therefore, these pollutants still can be generated. Quartz filters that strongly absorb wavelengths below 260 nm (the wavelengths that form ozone) can be used to reduce ozone generation.

HOW ARE EMISSIONS FROM UV/EB-CURED MATERIALS MEASURED?

VOC content of **coatings** is measured by EPA Reference Test Method 24. This method can be found in Title 40, Code of Federal Regulations, Part 60, Appendix A. For your convenience, Method 24 is provided in Appendix C of this report. Section 3.2 of Method 24 addresses non-thin-film **UV Radiation-cured Coatings**. This method is based on an American Society for Testing Materials (ASTM) test method (D 5403-93). If the amount of **UV coating** or **ink** as applied to the sample **substrate** is less than 0.2 grams (based on manufactures recommended

film thickness) and the area of the sample **substrate** is equal to or greater than 35 in² (225 cm²) then the **coating** is considered a thin-film **UV radiation-cured coating** for determining applicability of ASTM D 5403–93. No test method is specified for thin-film **UV coatings, inks** or **adhesives** or any **EB-cured materials**.

In considering and evaluating the modifications to Test Method 24 that eventually added procedures for testing non-thin-film **UV coatings**, minimum **VOC** content was found when a **resin** was **UV-cured** well beyond the manufacturers recommendation.¹⁶ The supporting paper evaluating this modification did not state whether the recommended cure was intended for an oxygen-free atmosphere, or whether an oxygen-free atmosphere was used. Because it made no mention of a **nitrogen blanket** to exclude air from the curing process to minimize **oxygen inhibition**, we assume that one was not used. **Oxygen inhibition** of a cure in atmospheric air would explain the need for a higher **UV** dose (i.e., the amount of **UV radiant energy** required to complete the cure and assure minimum **VOC** emissions). The report also stated that lamp output power in the test apparatus was not measured, and that there is no easy relationship between the power input level and **UV** light output at the specific wavelengths that cause a **coating** to cure. Therefore, low lamp output at the desired wavelength also could have increased the cure time.

Manufacturers of **UV radiant energy** cured materials believe that Method 24 overstates **VOC** emissions because it subjects a cured **UV** material to excessive heat (110 +/- 5°C) after a cure. Manufacturers suggest that excessive heat causes a **UV coating** to decompose and that a resultant loss of **coating** mass is being reported as **VOC**. EPA is aware of these concerns, but has no plans to revise the test method or develop a new method at this time.

WHAT ABOUT WORKER HEALTH AND SAFETY?

There are three major worker health and safety issues that need to be addressed: (1) potential exposure to **UV/EB radiation**; (2) potential exposure to hazardous components that are part of **UV/EB-cured materials**; and (3) hygiene to protect workers. This section will discuss all of these issues and significant changes and improvements made over the past ten years to minimize potential hazards.

What Health and Safety Concerns Does UV/EB Radiant Energy Present?

UV radiant energy is **ultraviolet** light. This is the same type of **ultraviolet** light that is received from the sun. It cannot penetrate the skin, but can cause sunburn and tanning of the top layer of skin or can cause eye irritation. When properly shielded, **UV** does not cause even these to occur.

EB radiant energy consists of high velocity electrons and subsequent **x-rays**. Electrons are generated in an accelerator or gun that projects them toward the **coating, ink** or **adhesive** and the **substrate**. Electrons generate **x-rays** as their speed is retarded in these materials, and by any

molecules between the **EB** source and the target film and **substrate**. Manufacturers of this **EB** equipment install shielding to reduce x-**radiation** to below background level.

According to OSHA regulations (Code of Federal Regulations (CFR) part 1910.96), no employer shall possess, use, or transfer sources of **ionizing radiation** (OSHA's definition excludes **UV**) in such a manner as to cause any individual to receive, in any quarter of a calendar year, more than:

Whole body, head and trunk, active blood-forming organs, or gonads.....	1.25 REM
Hands and forearms, feet and ankles.....	18.75 REM
Skin of whole body.....	7.5 REM

An individual can receive a dose greater than this if:

1. During any calendar quarter the dose equivalent of the whole body does not exceed 3 **REM**.
2. The dose equivalent to the whole body when added to the accumulated dose equivalent to the whole body shall not exceed 5(N-18) **REM**, where N equals the individual's age in years.
3. The employer maintains past and current records which show that the addition of such dose equivalent will not cause the individual to exceed the above tabulated amounts.

Additional limitations may exist in the form of local, state, or subsequent federal regulations. It is the responsibility of the employer to determine what regulations apply and to assure that employees are not exposed to **ionizing radiation** that exceeds statutory and regulatory limits.

How Can Workers Be Protected Against UV/EB Ionizing Radiation?

The principal means of protection from all **ionizing radiation** is shielding. This shielding is integrated into **UV/EB**-curing equipment in most cases. In the event of **UV** leakage, clothing is a backup to shielding and wearing full sleeved and full legged garments is recommended. Eye protection with side-shields is also recommended for the same reason.

With **near-UV**, **far-UV**, and actinic **radiation**, shielding consists of opaque barriers and baffles. Baffles are needed because **UV radiation** can readily scatter from sub-micron aerosols and become a diffuse glow reflected and re-radiated from aerosols and surfaces. **UV** can scatter much more readily than visible light can, because its wavelength is shorter and sub-micron aerosols in air can readily scatter **UV**. These aerosols are invisible (too small to be seen) because they fail to efficiently scatter visible light. Multiple baffles are needed to reduce the leakage produced by this scattering before it reaches human tissue. OSHA allows up to 1 milliwatt/square centimeter of **near-UV radiation** for exposure times over 16 minutes. OSHA allows only up to 0.1 milliwatt/square centimeter of actinic **radiation** for 8 hour exposures.¹

Unlike **UV** with coexisting visible wavelengths, **electron beams** and **x-rays** have no visible component to alert a human being to their existence. Because human genes (just like the **photoinitiator**, **monomer**, and **oligomer** molecules) are sensitive to molecular breakage under **ionizing radiation**, workers need to be shielded from **EB radiation**. Ideally, **radiation** intensity should be reduced to near background **radiation** level by shielding. The background **radiation** level is the intensity of **x-ray** and gamma **radiation** that would exist if no **radiation** source (except for trace sources of naturally radioactive materials) were close enough to affect the **radiation** intensity. There are many of these low-level natural sources (such as wood, wood-fiber, paper, metals, and masonry) and therefore the background level can never reach absolute zero.

At wavelengths of **x-ray** and shorter, scattering becomes pronounced and there is no truly opaque material. The mass of a shield will attenuate (reduce) the intensity of **radiation** that penetrates that shield, as will the **atomic number (Z)** of the material. Higher **Z** materials attenuate penetrating **radiation** more than low **Z** ones of equal mass. However, the first solid to be encountered by **radiation** should be a low **Z** material, both to minimize generation of **x-rays** and to absorb **x-rays** that are generated from the higher **Z** materials that are encountered later in a multiple layer shield.

X-ray and shorter wavelengths are usually shielded by lead, other heavy metals, concrete, or distance. In the absence of shielding, **radiation** intensity is reduced by the square of the distance between the source and the point of the measurement. Obviously, nobody can afford to place an operator a kilometer or even a hundred meters away from a source just to attenuate the intensity and limit the dose they receive. Shielding which places a high-**Z** mass between a source and a person is used to attenuate (reduce or weaken) **x-rays** within a reasonable distance. This shielding must include baffles to limit leakage of scattered or re-radiated **x-rays** because even air molecules and aerosols can scatter **x-rays**. The effectiveness of shielding must be tested by measuring the **radiation** level to assure that **radiation** leakage is near background levels while an **electron beam** is operating.

What Health and Safety Concerns Do Hazardous Components in UV/EB-Cured Materials Present?

The toxicity of constituents that are vapors and gases are determined from the MSDS that are required to be supplied with a **coating**. According to OSHA regulation 1910.1000:

$$E = C(a) T(a) + C(b) T(b) + \dots C(n) T(n) \text{ divided by } 8$$

Where:

E is the exposure in terms of effective concentration.

C is the concentration during any time period T where the concentration remains consistent.

T is the duration in hours of the exposure at concentration C.

The value of E shall not exceed the 8-hour time weighted average specified in Subpart Z of 29 CFR Part 1910 for the substance involved. Table Z-1 (which is too large to insert here) gives the permissible exposure limits (PELs) which are 8-hour time weighted averages (TWAs) unless otherwise noted. A “C” designation on concentration in the table denotes a ceiling limit on the concentration.

When **monomers**, **oligomers** and **photoinitiator** have become part of a **polymer**, they no longer have the toxicity that they previously had. Therefore, the **UV/EB radiant energy** can be considered as transforming the composition of a liquid material and thereby changing its toxicological properties. This transformation generally reduces toxicity by making the contribution of each component to overall toxic dosage unavailable.

Monomers that were used with acrylic **functional groups** over 20 years ago were toxic at a dose of milligrams per kilogram of body weight. Everything is toxic, it just depends on the dose. You can be killed by ingesting even pure water or table salt if the dose is large enough. **Acrylates** in use today have a greatly increased **toxic dose** (which means a lower toxicity) when compared to **monomers** and **photoinitiators** used in the past. However, these formulations should still be used with adequate hygiene (safety precautions). Table 4 lists some allowable emissions that were found in 1991.

Additional compounds could have been listed in Table 4, but no PEL standards were available for them in 1991. These unlisted compounds include: acetophenone, benzophenone, caprolactone **acrylate**, 2,2 dimethyltrimethylene **acrylate**, epoxy **acrylate**, ethoxyethoxyethacrylate, ethoxyethyl **acrylate**, 2 ethylhexyl methacrylate, glycerolpropoxytri**acrylate**, hexandiol **acrylate**, methylcarbamoxyloxyethyl **acrylate**, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane tri(3-mercaptopropionate, tripropyleneglycoldiacrylate, n-vinyl pyrrolidone. The fact that there were no standards available indicates the infancy of **UV/EB** materials in 1991.

Table 4 Permissible Exposure Limits of Radiation-Curable Material in 1991

Compound	8 hour time averaged permissible exposure limit (PEL)
1,4 divinyl benzene	10 ppm
2-ethylhexyl acrylate	50 ppm
hydroxypropyl acrylate	0.5 ppm *
phenyl glycidyl ether	10 ppm
styrene	100 ppm
vinyl cyclohexene dioxide	10ppm

Note: * - There were no federal standards available, values recommended by American Conference of Government Industrial Hygienists (ACGIH). OSHA determined the PEL.

Ten years ago, many **photoinitiators** were **VOC** and leached out after **polymerization**.³⁰ Because these **photoinitiators** also were toxic, they were undesirable and not allowed to contact food. As a result, new **photoinitiators** were developed that replaced the old ones. These new **photoinitiators** have a lower toxicity in an uncured state and become an integral part of the **polymer** molecule. Therefore, toxic compounds can no longer migrate or leach out. After **polymerization** they are no longer separate and toxic molecules.

The Toxic Substance Control Act (TSCA) of 1977 gave EPA broad authority to assess risks to human health. Most of the **radiation**-curable materials were subject to TSCA. Section 5 of TSCA required manufacturers or importers of a new chemical substance to submit a Pre-Manufacturing Notice (PMN) for a new chemical substance (NCS) 90 days prior to its manufacture or import. During the 90 day period, EPA had to decide whether or not the NCS presented an unreasonable risk. In 1991, questions about acrylic material caused few if any **acrylates** to clear the PMN step of the regulatory process. This inhibited the development of **acrylates** and also inhibited the development of alternatives. However, a study by the Specialty **Acrylates** and Methacrylates Panel of the Chemical Manufacturers Association changed that situation. Based on that study, the EPA's position changed and the EPA no longer automatically considers newer **acrylates** and methacrylates as significant health risks. However, if a new **acrylate** is structurally similar to a substance for which EPA has positive toxicity data, EPA may regulate that substance on the basis of its potential risk. This change in EPA policy has helped to introduce new **acrylates** and methacrylates, especially those with higher molecular weight. Therefore, the toxicity of **UV/EB**-cured **monomers**, **oligomers** and **photoinitiators** are much less of a concern today than they were in the past.

The American Industrial Hygiene Association has published Workplace Environmental Exposure Levels (WEELs) for several **monomers** used in **UV/EB**-curable **coating** technology.¹ Table 5 shows the PELs for organic **solvents** that could be used for cleanup or dilution.

When applying a **coating** by spray painting, about 50% of the **coating** is carried away in air flow as **overspray**. This amount of **overspray** can be as small as 10% if electrostatic deposition is used. This is true of both conventional paints and **UV** paints. The conventional and **UV** paints can have a comparable toxicity prior to curing. However, all of the **overspray** of a conventional paint must be disposed of, because it has flashed off its volatile components (mainly the **VOC**) and changed its viscosity. The **UV** paint that is captured by the arrester can be reused because it typically contains no volatile **solvent** and, therefore, has not changed its viscosity.

Paint **overspray** arresters (filters in the air exhaust from a paint spray booth) capture 90% to 99% of the **overspray** droplets. Reuse of **overspray** droplets that drain off of a **UV/EB** paint **overspray** arrester can increase the overall effectiveness of a spray **coating** operation. Various types of paint **overspray** arresters, when used with conventional paints, allow droplets with aerodynamic diameters from 3 to 7 microns or less unimpeded passage. However, a filter to capture droplets down to 1 micron in diameter could be used with **UV** paints. This is practical because drainage from the filter in a **UV** process can be reused and the cost realized, as a

TABLE 5: PERMISSIBLE EXPOSURE LIMITS (PEL) FOR ORGANIC SOLVENTS

Compound	8 hour time weighted average permissible exposure limit (PEL)
n-butoxyethanol	50 ppm
butyl acetate	150 ppm
n-butyl glycidyl ester	50
butyl lactate	5 ppm *
p-tert-butyl toluene	10 ppm
carbon tetrachloride	10 ppm
di-isopropyl ether	500 ppm
n,n dimethylacetamide	10 ppm
dipropylene glycol methyl ether	100 ppm
dipropyl ketone	50 ppm
2 ethoxyethanol	200 ppm
2 ethoxyethyl acetate	100 ppm
ethyl acetate	400 ppm
ethyl butyl ketone	50 ppm
ethyl ether	400 ppm
sec-hexyl acetate	50 ppm
isophorone	25 ppm
isopropanol	400 ppm
isopropyl acetate	250 ppm
mesityl oxide	25 ppm
methyl acetate	200 ppm
methylal	1,000 ppm
methyl alcohol	200 ppm
methyl n-amyl ketone	100 ppm
methyl n-butyl ketone	100 ppm
methylcyclohexane	500 ppm
methyl ethyl ketone	500 ppm
5-methyl-3-heptane	25 ppm
methyl isoamyl ketone	50 ppm
n-propyl alcohol	200 ppm
propylene glycol monomethyl ether	100 ppm *
1,1,2,2-tetrachloroethane	5 ppm
tetrahydrofuran	200 ppm
toluene	200 ppm
xylene	100 ppm

* Note: No Federal Standard, value recommended by ACGIH

result of the greater pressure, would be less than the cost of the paint saved.

To minimize potential exposure to uncured **UV** droplets that do pass through the arrester, a **UV**-curing unit should be installed on an arrester exhaust. If a **UV**-curing unit is used to cure the droplets that pass through the filter before they are exhausted to the atmosphere, the aerosol in the exhaust air would not be toxic. In addition, the cured exhaust stream would be less likely to mark a neighbor's roof than an aerosol from a conventional spray booth.

A paint **overspray** arrester is typically removed when it is "fully loaded" with uncured conventional paint. "Fully loaded" means that a filter has too great a pressure drop when passing the required air flow. In addition to a "fully loaded" filter (and the paint it contains), paint that has drained off the **overspray** arrester must be considered. When a conventional paint is used, this drainage cannot be reused because it has flashed off its volatile components and is more viscous than the sprayed paint. Therefore, with conventional paints, a greater amount of waste must be handled and this poses a greater threat of adverse health effects. This threat of adverse health effects can be minimized by using and reusing **UV** paint.

The aerosol emission of mist was noted in 1991 as "**monomer** emissions", for which the quantity and composition of emissions were to be researched. It has since been discovered that this aerosol or mist is emitted not only from spray guns, but from rollers and printing presses (especially high speed operations). Misting varies from 1% to 50% of the total consumed **UV/EB coating or ink**. If misting is a problem, the equipment, process and materials suppliers can work with operators to minimize emissions.

Conventional **coatings** can range from 40% to 80% **solvent** by volume. This **solvent** is frequently a combination of **VOC**. Ingredients in conventional **coatings** that cause health effects include **HAP**, **VOC**, and pigments. **HAP** include ingredients that are toxic, neurotoxic, and carcinogenic. **UV/EB** materials essentially do not contain **VOC** or **HAP** (Currently available **UV/EB coatings** may have **HAP** as a very minor ingredient that becomes part of the **polymer**). Some pigments have displayed toxicity.

Currently available **UV/EB coatings** emit only 1% - 5% by weight, while older **coatings** could emit up to 10% as curing volatiles. These values are based on Method 24 results. Method 24 bakes the **coating** after the cure to drive off any residual **VOC**, but this may cause some decomposition to occur.

What About Worker Hygiene?

Hygiene is the procedure that is followed to keep from getting injured, sick, or otherwise having health problems. It is contrasted with therapy, the procedure followed to recover or to get well after you have gotten injured, sick, or developed a health problem. Hygiene is safety precautions. Therefore, it is a good idea to follow good hygiene, even though you may not agree

that it is necessary, or understand why it is required.

Several regulations or laws have been enacted, including the Federal Hazard Communication Standard, plus federal, state, and local laws and regulations requiring workmen to be informed of risk factors in a job. Parts of these standards regulate product warning labels, MSDS, worker education, and training. These standards should help you understand why hygiene needs to be practiced, why specific hygienic practices are required, and how to communicate hygiene requirements to employees.

Although **UV/EB**-curable materials, in their modern form, have not been in use long enough to demonstrate long-term toxic effects, some older **UV/EB** materials have demonstrated short-term toxic effects. These short-term effects have abated somewhat with development of less toxic materials over intervening years since these effects were observed.

Because the same base **monomers** and **oligomers** are used in conventional **coatings**, **inks** and **adhesives** for painting or printing, **UV/EB** materials are subject to the same conventional painting or printing hygiene with some additions. Some of these additional safety precautions are attributed to the acrylic group (or other **functional group**) which has been attached to an **UV/EB**-curable molecule. An acceptable risk of occupational contact dermatitis (inflammation of the skin and mucous membranes) and eye irritation can be achieved with proper protective clothing, proper handling procedures of **UV/EB**-curable materials and proper shielding from **UV/EB radiation**. Contact dermatitis also may be caused by an allergic reaction to a substance in a **UV/EB** material that is only present in trace amounts.

It is important to remember that **UV/EB**-curable materials remain spreadable and not necessarily in one place until they are cured or cleaned up. They do not evaporate, cure, or dry up like conventional materials do. They may travel based on contact, first from a contaminated site and then on contact to any other site. Equipment touched by contaminated gloves will remain contaminated and a source of exposure until it is either exposed to **UV/EB radiation** or cleaned up.

UV/EB-curable materials should never be allowed to come in contact with the eyes. For eye protection, safety glasses, goggles, or a full face shield should always be worn when handling any chemicals or **solvents** (See Figure 13). This was especially true of older **UV/EB** chemicals, but you should use this precaution even though newer **UV/EB** chemicals cause less eye irritation and are less toxic.

You should never look directly at **UV** lamps or strong reflections, even with eye protection. All eye protection materials should have side shields and absorb sufficient **UV** light to prevent unintentional exposure and the resulting eye irritation.¹

You should never adjust **UV** or **EB** shielding without qualified supervision.¹

You should always eat or drink in a designated lunch area, and never in the work area. You should be alert to any contamination of this area and avoid such contamination. You should also wash thoroughly before touching any food or drink.²⁴ You should apply a barrier cream after eating and before returning to work.

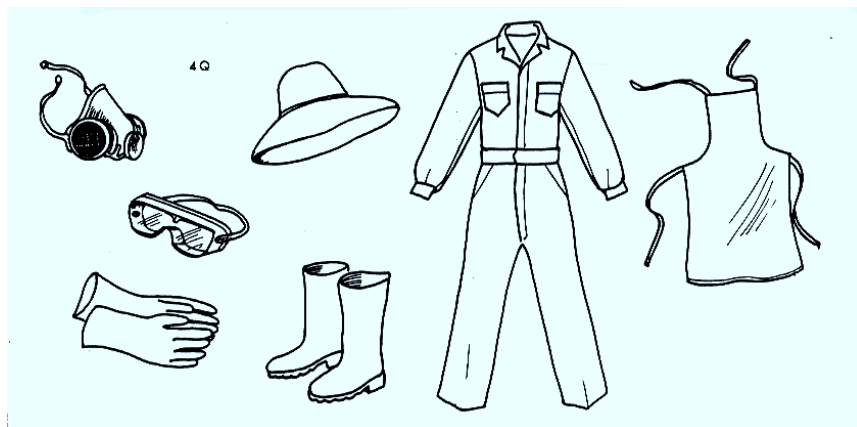


Figure 13: Examples of Safety Equipment

Direct skin contact with all **coatings**, **inks** and **adhesives** should be avoided.¹ Always wash hands thoroughly before using restroom facilities. Barrier cream should subsequently be reapplied after washing hands and before returning to work.²⁴ Barrier creams should be applied to clean skin before exposure and not applied after exposure. Barrier creams can protect against material that might penetrate through defects in the protective equipment.

Typically, fabric or non-woven long sleeved and full leg clothing or coveralls are worn. Rubber gloves should always be worn when direct contact with **radiation** curable materials is possible. It is appropriate to use the same hygiene for **UV/EB** materials that you would use for a **solvent**, a corrosive chemical, or a toxic chemical. Wearing protective clothing for a full shift may also require that air temperature be controlled to allow workers to remain comfortable. Use of a rubber apron or rubber suit is appropriate when there is a possibility that you could be splashed with **solvent**, corrosive, or toxic material. Shoes must provide full foot coverage. Rubber boots should be worn when there is danger of a spill or when walking where a **solvent** or toxic material has spilled.

Contaminated leather objects (shoes, belts, etc.) should be discarded because they cannot be decontaminated. Always change work clothes before leaving the plant. Never wear the work clothes or the work shoes away from the plant.

Contaminated clothing can be laundered at a commercial laundry, but not in a home laundry. After cleaning, they may be worn again. Heavily contaminated clothing should be discarded.²⁴ Rags used for clean up should immediately be placed in a container for either disposal or laundering and should never be placed in your pocket.¹

Some **coatings** use **monomers** and amine **photoinitiators** that may have strong odors. Vapor inhalation is usually an odor problem, but could also become a toxicity problem. Therefore, ventilation for odor control is strongly advised. Although odoriferous amines are falling out of

use, ventilation should also be used for mist aerosols, ozone, and **HAP** that might result when **UV/EB radiation** cured materials are applied and cured. Odors can reach concentration levels that require controls for the comfort and, perhaps, health of workers.

Misting occurs in high speed presses, at liquid **ink** transfer points, when paints are sprayed and during application with high speed rollers. Mist is an aerosol that is probably toxic and possibly carcinogenic. Misting forms deposits in **UV** lamp enclosures. Such deposits reduce **UV** output and increase heating within an enclosure. Electrical arcing can occur at lamp electrode contacts as a result of powder accumulating due to misting. This can cause slower curing speeds and result in higher operating costs. Deposits must be removed from ovens and lamp enclosures with a mild detergent to avoid these problems.

The droplet size of mist aerosol is often smaller than 3 microns, but can be larger for sprayed paints. In both cases, its existence is well-known. Since uncured **UV/EB** materials have a toxicity, prudence would require that you not breathe this aerosol. A suitable filter mask or supplied air mask is recommended when there is no ventilation. If an aerosol has been cured by sufficient exposure to **UV** or **EB radiant energy**, it no longer is toxic. Operations that produce such aerosols or mists should be enclosed and well ventilated. Ventilation should carry air to an **ultraviolet** light source or sunlight to cure a **UV coating** or **ink** aerosol, because droplets are frequently too small to be filtered out. Such aerosols should not be emitted after sundown unless cured by a curing unit before being emitted. Aerosols can also form in a fire, or with uncontrolled **polymerization** of bulk materials. A mask providing fresh air or an organic vapor respirator should be worn under such potential exposure conditions.¹

Make sure that you do not exceed the allowed exposure to **ionizing radiation**. While the OSHA definition only applies to **x-rays**, care must be taken to assure that workers do not receive a **UV** dose that would irritate either their skin or eyes.

COST CONSIDERATIONS

ARE UV/EB-CURED MATERIALS MORE EXPENSIVE THAN CONVENTIONAL COATINGS, INKS AND ADHESIVES?

Conventional **coatings**, **inks** and **adhesives** can emit 50% to 80% of their volume as **VOC**. This **VOC** evaporates and is carried away by ventilating air flow from application processes and/or from thermal ovens that dry and cure this material. **VOC** emissions from **UV/EB**-cured materials are much less, ranging from 1% to 10% of the weight of the **UV/EB** material. Typically, **VOC** emissions from most **UV/EB** material applications are less than 5% of the applied material weight. Also note that virtually every component in a **UV/EB**-cured material becomes part of the cured **coating ink** or **adhesive**, but only 20%-50% of a conventional material (i.e., the **resin** and pigments, not the **solvent**) becomes applied **coating** solids. Less gallons of **UV/EB** material are needed to cover the same amount of area at the same film thickness. Therefore, the best way to compare the cost of **UV/EB** and conventional materials is on a solid film basis instead of cost per gallon.

More effective use of **UV/EB**-cured materials (based on reuse of **overspray**) can make **UV/EB** operations more cost effective than conventional operations. In addition, more cost savings result when using **UV/EB** technology as a result of lower energy requirements, reduced floor space, increased productivity and absence of add-on control equipment. **Overspray** of **UV/EB** materials can be effectively captured and reused because they generally lack volatiles, and will not cure unless exposed to **UV/EB radiant energy**. If recirculation of **UV/EB** material is a viable alternative, the cost of **UV/EB** materials could actually be about 30% - 60% of the cost of a conventional **coating** on a comparable solid film basis (this is for material cost only).

The cost of “as applied” **UV/EB**-cured **coatings** is about 15% greater than conventional **coatings** on a per gallon basis. However, as noted above, over half of a conventional **coating** evaporates and does not become part of the final cured **coating**. Because **UV/EB**-cured **coatings** have only a 1 to 10 % loss, they cost about 45 % less than conventional **coatings** per square foot on a solid film basis. The 1991 CTC report stated that **UV/EB coatings** cost as much as four times the cost of conventional **coatings** on a per gallon basis, and twice as much on a solid film basis. Over the past 10 years these differences are no longer valid because of reductions in price of **UV/EB**-cured materials. When higher production rates (along with a resulting reduction of inventory in-process), lower energy consumption and reduced floor space requirements are considered, economic considerations greatly favor **UV/EB** over conventional **coating** technologies in most cases. Similar economic advantages are found in the printing industry.

Higher production rates for **UV/EB** processes are based on shorter (faster) cure time. Shorter cure times result in smaller curing units (compared to conventional thermal dryers) that require less floor space (See Figure 14). Also, there may be additional space savings because **UV/EB**-cured products do not require conditioning time in storage. For conventional processes that use thermal ovens, product exiting an oven may have to be held for several hours (8 to 24 hours or possibly more) in storage if conditioning of the **substrate** is necessary (e.g., to reduce brittleness after a paper **substrate** has been subjected to heat and drying in an oven). This conditioning often requires storage at controlled temperature and humidity. This type of storage is not needed for products after **UV/EB**-curing. Therefore, **UV/EB** processes may have an additional space and productivity advantage over conventional operations that require product conditioning after exiting a thermal oven.

As an example, consider two printing lines with 10 foot wide **webs** and operating at 1,000 feet per minute. One printing line uses **UV** technology and print leaves the curing unit completely cured. The other printing line uses conventional technology and print leaving the oven is sufficiently cured (i.e., it will no longer smudge). In this comparison, the conventional material must reach that point in 6 seconds in an oven that extends 100 feet. This may be optimistic. The conventional process may have to run slower than this, but we will assume that the conventional material will cure sufficiently in 6 seconds. By comparison, the **UV** cure will take a fraction of a second and the **UV**-curing unit only takes up 100 square feet. The thermal oven will need to use 1,000 square feet (10 x 100) of rental floor space at \$0.50 per square foot per month (\$6.00 per square foot per year), for a total of \$6,000 per year. The **UV**-curing unit will use only 100 square feet (10 x 10), and the rental cost is \$600 per year.

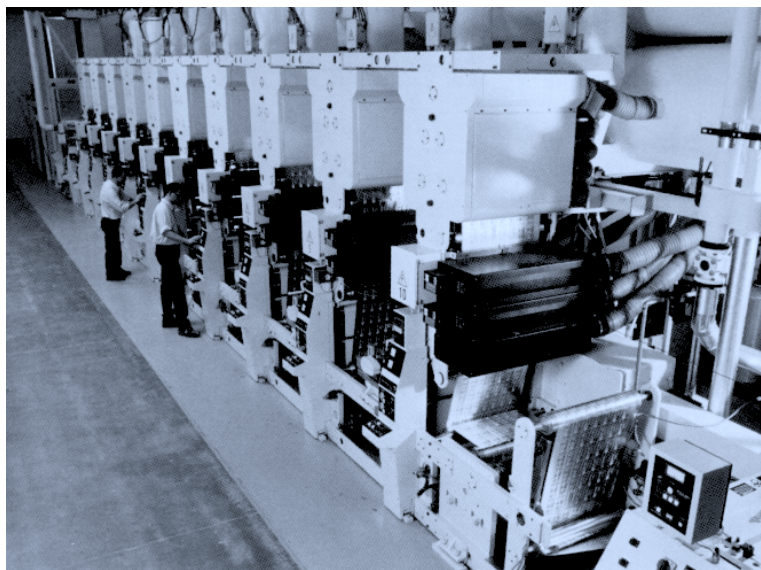


Figure 14: Presses With UV-Curing Units

For the same example, energy consumption for a thermal oven is 1.5 MBTU/hr plus blowers at 56 kW. We will assume that natural gas consumption will be at \$3.00 /MBTU and electric consumption will be at \$0.07/kW-hr. If the plant operates 300 days per year for two shifts, the total energy cost for the thermal oven would be \$21,600 per year and the cost of electricity for the blowers would be \$18,816 per year. In comparison, the UV-curing unit would use 5.6 kW/lamp times 12 lamps times \$0.07/kW-hr to cost \$22,579 per year and ventilation would cost \$336 per year on the same basis.

In summary, the cost of operating a conventional printing line in the example would be \$6,000 + \$21,600 + \$18,816 = \$46,416. The cost of operating the UV printing line would be \$600 + \$22,579 + \$336 = \$23,415. This is a savings in operating cost for the UV line over the conventional line of at least \$23,001 (\$46,416 - \$23,415), or about 50% for this hypothetical example.

The capital cost of a thermal oven is significant. The capital cost of a UV-curing unit is almost trivial by comparison. Even an EB-curing unit should cost less.

As previously indicated, UV/EB-cured **coatings, inks and adhesives** cure rapidly and can go on to the next finishing operation in the production process immediately. The only exception (at this time) is if **cationic photoinitiators** are used. **Cationic** curing takes a few seconds compared to almost instantaneous cures when using **free radical photoinitiators**

The cost of add-on emission control technology for conventional **solvent** (i.e., **VOC**) based **coatings, inks and adhesives** can be from \$250,000 to over \$3,000,000. UV/EB-cured **coatings** have minimal **VOC** emissions; therefore, add-on controls are not required. The capital and

operation and maintenance costs of the emission controls needed for conventional applications should be included in any comparative cost analysis.

When **UV/EB** materials are used, fire insurance premiums should be reduced due to the lack of inflammable **VOC**. (One insurance company reported a 5% reduction). The absence of inflammable **VOC** at facilities using **UV/EB** technology should reduce accidents that lead to fire or explosion.

Protective equipment and safety measures that must be used with **UV/EB** materials are typical of the chemical, printing, painting, and **coating** industries in general. Although there may be some variation in safety precautions between facilities that use **UV/EB** materials compared to conventional materials, the variations should not greatly influence cost.

The actual costs for implementing **UV/EB** technology for a particular operation will vary with time and circumstances. Actual cost estimates should be obtained for each facility and process at the time a change is being considered. The net cost of a change to **UV/EB**-cured technology usually allows payback within two years.

SUMMARY

WHAT ARE THE ADVANTAGES OF USING UV/EB-CURED COATINGS, INKS AND ADHESIVES?

- ★ Cures Fast - Runs at higher rates and cures in a shorter time than evaporative **coatings**.
- ★ Low Energy Consumption - Uses much less energy to cure than evaporative **coatings**.
- ★ Compact Design - Uses much less floor space than conventional evaporative **coatings**.
- ★ Low Emissions - Less emissions without controls than most conventional evaporative **coatings** systems with emissions controls.
- ★ Regulatory Advantage - Easily meets most regulatory requirements and eliminates some.
- ★ Cost Effective - Reduces initial costs and payback times. No conditioning required.
- ★ Produces High Quality Finish - Used for quality furniture, magazines, microelectronics.
- ★ Ready-to Go - Materials supplied ready to use - no blending/mixing required.
- ★ Reusable/Recyclable - No volatiles lost in application, can be reused immediately.
- ★ Cures in Curing Unit - Does not cure on equipment, can be left over a weekend.

- ★ Less Worker Exposure to **HAP/VOC** - Absence of **HAP/VOC** in **UV/EB** materials.
- ★ Less Flammable - Greater safety, lower fire insurance premiums.
- ★ Able to Recycle Product - Paper from **UV/EB** products can be recycled, even to higher grade

WHAT ARE THE DISADVANTAGES OF USING UV/EB-CURED COATINGS, INKS AND ADHESIVES?

- Misting/**Overspray** - Spray and high speed roller and printing applications can produce aerosol that can be inhaled.
- Aerosol Toxicity - Aerosol is uncured, toxic, and will not go away without cleanup.
- Worker Hygiene/Sensitization - Similar to other processes, but different. Has different results.
- Workplace Contamination/Cleanup - Contamination will persist and spread until cleaned up.
- Persistent in Environment - Uncured material will persist in shade.
- **UV/EB Radiant Energy** - Can injure if used improperly.
- Customer Resistance - Historic risk of not meeting need. This may now be past.

CONCLUSIONS

1. **UV/EB-cured coatings, inks and adhesives** are widely used and are expected to be more widely used as people become more familiar with this material and developers produce new, safer, and better **coatings, inks and adhesives** to apply to specific objects or **substrates**.
2. Toxicity of **UV/EB-cured coatings** has gone from very toxic to only mildly toxic. Further advances in toxicity reduction are anticipated. Conventional **coatings** are considered mildly toxic. Cured **coatings** of all types are usually free of toxicity.
3. Use of **UV/EB-cured coatings, inks and adhesives** requires good hygiene in handling and disposal of waste. This hygiene is similar to what is already used in the **coating, printing, and chemical industries**. However, each situation requires somewhat different equipment.
4. Using **UV/EB radiant energy** to cure instead of heat to evaporate **VOC** from **coatings and inks** reduces energy consumption, fire hazard, need for control technology, in-process product storage requirements, floor space needs and, probably, insurance premiums. These reductions should provide potentially significant economic benefits.

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GLOSSARY OF TERMS

Acrylate(s)	An organic salt (an ester) produced by the reaction of acrylic acid with an organic molecule. It is any molecule that has an acrylic radical attached to it.
Actinic UV	Actinic or far-UV (both terms mean the same thing) is the UV radiant energy between 180 - 315 nanometers in wavelength. It is used mainly for sterilization. Also see UV Radiant Energy .
Adhesive(s)	Specialty coating designed applied to a material to make it cling or stick fast to another surface (e.g., the coating applied to make pressure sensitive tape and labels).
Arrhenius Acid(s)	S. Arrhenius of Sweden defined an acid as a hydrogen ion donor. Since the hydrogen ion is a proton and a neutron, this is very close to a Bronsted acid . Also see Lewis acid .
Atomic Number (Z)	The number of protons in the nucleus of each atom of an element. The atomic numbers for naturally occurring elements range from 1 to 89. Man-made elements exist above this range.
<i>Bremsstrahlung</i>	In German, <i>Bremsstrahlung</i> is literally retarding or braking radiation . <i>Bremsstrahlung</i> is the energy lost in the elastic impact of electrons, or the energy lost when an electron goes from a larger orbit to a smaller orbit. It is radiated as x-rays .
Bronsted Acid(s)	J. N. Bronsted of Denmark defined an acid as a proton donor. This definition allows an organic radical or a zeolite to be included with the acids. It replaced the concept of a hydrogen ion donor for chemicals that do not hydrolyze or generate hydrogen ions. See also Arrhenius acids , Lewis acids
Catalyst(s)	There are two types of catalysts , heterogenous and homogenous. Both affect the rate of chemical reactions. A heterogenous catalyst is a substance within another phase (solid, liquid or gas). A homogeneous catalyst is a substance within the same phase. Heterogenous catalysts do not enter into the reaction, but homogeneous catalysts may enter into the reaction.
Cationic/Cationic Polymerization	A positive valence ion that is attracted to the cathode in electrolysis. A cationic photoinitiator is one that decomposes under UV/EB radiant energy or from Bronsted Acids to form cations that cause polymerization to occur by an ionic mechanism.
Coating(s)	A protective, adhesive , or decorative film applied in a layer to a surface. The coating can be applied as either a liquid or a solid.

Crosslinking	The interconnecting of one polymer molecule with another by molecular bonds. Crosslinking raises the glass transition temperature and gives mechanical strength and abrasion resistance to the polymer .
Diluent(s)	A low viscosity chemical that is added to a mixture to reduce overall viscosity. This includes reactive diluents that become part of the polymer molecule upon polymerization . Reactive diluents may be VOC prior to polymerization , but cease to be VOC after polymerization
Dimer(s)	Two identical molecules link together to form one molecule. An example is a hydrogen peroxide molecule which is two hydroxyl radicals linked together.
Electromagnetic Wave(s)	Radially propagating energy in the form of photons or waves, traveling away from a source. These photons or waves are characterized by wavelength or frequency, amplitude, intensity, and quantum parameters. Wavelength is the speed of propagation divided by frequency. Amplitude of a wave is a measure of the strength of the energy. Intensity is measured as the rate at which the energy is absorbed.
Electron Beam (EB) EB Radiant Energy	Electron beams are produced by a high potential gradient between electrodes. When the gradient is high enough, electrons stream from the negative electrode. A positive electrode having a hole in the middle attracts the electrons. Because an electron has mass, electrons that are directed toward the hole continue through as an electron beam .
Excimer(s)	An excimer is an <u>excited dimer</u> . It is a molecule that is split apart by photons . It gives a defined spectrum of electromagnetic energy when the dimer reassembles. If two or more photons caused the split, the emitted spectrum can even be at a shorter, more energetic wavelength.
Far UV	See Actinic UV
Fluorescence	The phenomenon of a single photon exciting a molecule and causing that molecule to emit a longer wavelength.
Free Radical / Free Radical Polymerization	A free radical is a molecular fragment having a single unpaired electron. It causes polymerization by transfer of an electron from a monomer molecule. When this transfer occurs, the free radical and the monomer molecule become one. This new molecule is a larger free radical that can then transfer an electron from still another monomer molecule. This process can continue in a chain reaction that will form a seemingly endless polymer molecule (one composed of many monomers).

Functional Group(s)	A radical that has been attached to a monomer or oligomer molecule. A functional group causes a molecule to become excited more easily in the presence of free radicals and radiant energy. The most commonly used functional groups are the acrylic, methacrylic, vinyl ether, and methoxyacrylic radicals .
Gray	A unit of absorbed radiant that is equal to one Joule per kilogram.
Hazardous Air Pollutants (HAP)	A list of 189 chemicals identified in the Clean Air Act Amendments of 1990 as Hazardous Air Pollutants . See Appendix E
Ionizing Radiation	Radiation that can ionize a molecule. The term usually refers to the amount of radiation that will ionize oxygen in air; that is, radiation with a wavelength shorter than 253 nm (this includes actinic UV radiant energy generated in UV-curing systems and electrons and x-rays generated in EB -curing systems).
Infrared (IR) IR Radiant Energy	Electromagnetic radiant energy that is emitted by any body above absolute zero in temperature. It is absorbed and sensed as heat. It is emitted as a spectrum, which shifts its peak to shorter wavelengths as the temperature increases. The non-luminous portion of that spectrum is in the range from 700 to ~11,000 nm.
Ink(s)	A pigmented fluid or paste that is used as a writing fluid or the visible result in printing.
Lewis Acid(s)	G. N. Lewis defined an acid as a electron pair acceptor. See also the Arrhenius Acid and Bronsted acid definitions.
Monomer(s)	A molecule that self-assembles into a polymer . Each monomer is another vertebra in a polymer 's carbon backbone. The types of monomer that are available will define the properties of a polymer . Monomer molecules are named for their chemical structure (e.g., epoxy, polyester, urethane, silicone, etc).
Near-UV	UV radiant energy between 315 nm and 400 nm. Also see UV Radiant Energy .
Nitrogen Blanket	Nitrogen gas that covers the substrate like a blanket to exclude oxygen in the ambient atmosphere. It is used to avoid ozone generation, nitrogen oxide generation and oxygen inhibition of polymerization .
Oligomer(s)	A group of 3 to 5 monomer molecules that have been joined together to form a larger molecule. It behaves as a monomer would, but is usually less toxic.

Overspray	The solids portion of a coating from a spray applicator which fails to adhere to the part being sprayed or coated. UV/EB overspray may be droplets of liquid because virtually all of the UV/EB material can become a solid.
Oxygen Inhibition	The premature termination of a polymer molecule caused by the reaction of oxygen molecules with free radicals . When polymerization is terminated prematurely, polymer molecules are shorter and perform differently.
Photoinitiator(s)	A compound that forms free radicals or cations when subjected to UV/EB radiant energy . A photoinitiator is sensitive to a specific wavelength of radiant energy. Photoinitiators now become part of the polymer that is formed.
Photon(s)	According to quantum theory, a hypothetical massless particle that is used to explain some aspects of an electromagnetic wave . In quantum theory, the electromagnetic wave and the particle are the same.
Polymer(s)	A chain of many monomer molecules linked together. This chain can be thousands to millions of monomers long. The polymer chain tangles and bonds to other polymer chains. Commonly, a polymer is known as a plastic.
Polymerization	The process that forms a polymer from monomers and oligomers .
Radiation	Energy (in some form) emitted from a source, propagated radially along a line-of-sight, and absorbed. However, depending on the type and source of the energy, the effects of radiation on humans are very different
Radical	An ionized portion of a molecule. Normally these are anions and cations, depending upon whether they have a surplus or deficiency of electrons.
Radioactivity	A property of some atoms in which electromagnetic energy is emitted. The energy comes from an unstable ratio of neutrons to protons in the nucleus of these atoms. The nucleus will either spontaneously fission or fuse to reduce the energy. This occurs spontaneously and the energy is radiated away as gamma rays, x-rays , or other particles. Half of the atoms having such identity will fission or fuse within a well defined half life.
Reactive Diluent(s)	see Diluents
Resin(s)	A term used interchangeably with polymer .

Roentgens (R)	A unit of absorbed radiation . One Roentgen equals 100 ergs per gram.
Roentgen Equivalent for Mankind (REM)	A unit of absorbed dose for the human body. It is expressed in Roentgens (see above). It is the absorbed dose over the spectrum up to 100 nm. Since the REM is an integral (the sum) of all these wavelengths multiplied by the absorption at that wavelength, there are no conversion factors from other measurements.
Solvent	A liquid used in a paint, coating or ink to dissolve or disperse film-forming constituents and to adjust viscosity. It evaporates during drying/curing and does not become part of the dried film.
Substrate	The surface to which a coating is applied.
Three-Dimensional (3D)	Any object that has length, width, and depth dimensions. Such objects are capable of casting a shadow over some portion of their surface. With regard to UV/EB technology, this refers to the ability to minimize the effect of such shadows to provide for curing of the entire coating .
Toxic Dose	The lethal dose for 50% of laboratory animals (rats) that ingested the substance. It can also refer to the concentration that if inhaled leads to 50% death of laboratory animals.
Transfer Efficiency	The ratio of the amount of coating solids deposited onto the surface of the coated part to the total amount of coating solids used.
Ultraviolet (UV) UV Radiant Energy	That portion of the electromagnetic spectrum between 180 nm and 400 nm. This can be broken into near-UV (315 nm - 400 nm) and far-UV or actinic (180 nm - 315 nm). It can also be broken into UV-A (315 nm - 400 nm), UV-B (290nm -315 nm), and UV-C (220nm - 290 nm). Near-UV , UV-a , and UV-B are used for curing UV materials. Sunburn is caused by UV-A and UV-B . Actinic UV or UV-C is used for sterilization.
Volatile Organic Compounds (VOC)	Any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compound other than those that the Administrator of EPA has determined to have negligible photochemical reactivity. See Appendix D

Web	Any fabric, paper, plastic film, metallic foil, coiled sheet metal, or other products which are flexible enough to be unrolled from a large roll, coated by blade, roll coating , or rotogravure as a continuous sheet and, after cured, rerolled
X-Ray(s)	Electromagnetic radiation having a wavelength ranging from 0.1 nm to 40 nm. X-rays have a relatively low absorption, and therefore pass through solids. The attenuation (reduction) in intensity varies with the mass along that path, the atomic number of the material along the path, and the wavelength of the x-ray . Some high Z materials can reduce the x-ray to background levels with only a short path.

APPENDIX A

ULTRAVIOLET AND ELECTRON BEAM RADIATION VS. RADIOACTIVITY

Radiation is a very broad term. It can refer to the emission of rays of heat, light, radio waves, or sounds; however, it can also may refer to the emissions of rays by a radioactive substance. **Ultraviolet (UV) and electron beam (EB) radiation** are not the same as **radioactivity** and should not be confused. Hopefully this appendix will help you understand the difference. Niels Bohr's concept of the atom (i.e., a nucleus of protons and neutrons surrounded by orbiting electrons) is the basis for this appendix. We do not need to go any deeper into the realm of atomic structure.

RADIOACTIVITY

Radioactivity is a property of atoms that have an unstable ratio of neutrons to protons in their nucleus (i.e., have more than the minimum energy in the nucleus). Because these atoms have more energy than atoms with a stable nuclide (i.e., a favorable ratio of neutrons to protons), these atoms are unstable. The nuclei of these atoms spontaneously divide (fission, when the number of protons is greater than 82, which is the **atomic number** of lead) or combine (fusion, when the number of protons is less than 82) with well-defined half-lives. These fissions and fusions cause emission of electrons, alpha particles (two protons and two neutrons, a helium nucleus), beta particles (a positron or an electron), neutrons, protons, **x-rays**, and gamma rays. The half-life is defined as the time for half of the atoms to undergo either fission or fusion. Half-lives range from almost instantaneous to millennia.

Fission or fusion of these atoms can be greatly accelerated when they are bombarded by neutrons from a chain reaction. This happens when neutrons are sufficiently conserved within a critical mass. As far as we know, a critical mass occurs only in man-made nuclear reactors and in nature in the core of each star and planet. Even the Earth has a radioactive core and, therefore, we cannot totally avoid all **radioactivity**.

There are naturally occurring radioactive isotopes of elements (atoms having a defined **atomic number**, but having various atomic weights). These isotopes exist in trace quantities and are radioactive. **UV/EB radiation** does not change the concentration, rate of reaction, or number of such isotope atoms. Therefore, **UV/EB radiation** does not change naturally occurring **radioactivity**. **UV/EB radiant energy** does not make atoms radioactive.

Gamma rays are not used for curing **UV/EB** materials because they require much more shielding to attenuate the intensity of **radiation** to near background **radiation** levels.³⁵

UV/EB RADIATION

UV/EB radiation refers to electromagnetic energy moving radially (i.e., radiating) from a source. This energy is normally transmitted over a line of sight, but it experiences scattering when it strikes an object. **Ultraviolet radiation** exists in sunlight and is emitted, very weakly, by radioactive materials (except when they undergo a chain reaction - as in the sun or Earth's core - and elevate their temperature). Our principal natural source of **ultraviolet radiation** is sunlight.

The energy of a **photon** is inversely proportional to its wavelength. Scattering is a function of wavelength and the size of the object that produces scattering. When the diameter of an object (scatterer) is less than a tenth of the wavelength of the radiant energy, scattering is negligible. When the size of the scatterer becomes comparable to or larger than the wavelength of the radiated energy, scattering is enhanced. You can see an example of this with visible light in a smoky room. Visible light rays (400-700 nm wavelength) go radially as directed until they strike a scatterer (e.g., a smoke particle of about 1000 nm) that scatters the **radiation**. Each scatterer acts like a point source in scattering waves of **radiation** and, therefore, each scatterer appears to be a luminous source. All wavelengths of **radiation** behave like this, regardless of the source. **X-rays** have a short enough wavelength that even oxygen and nitrogen molecules become scatterers like the smoke described above.

Electron beams are composed of particles (electrons) that collide with other electrons and scatter, too. Electrons do not actually collide with electrons, but repel each other in close encounters that resemble collisions. **Electron beams**, in scattering electrons and impacting nuclei, generate **x-rays** similar to those emitted from radioactive materials, but these **x-rays** (like medical **x-rays**) cease to be emitted when the **electron beam** is turned off.

CONCLUSION

Since **UV/EB radiation** does not supply neutrons, the **UV/EB-cured** material does not have any change in **radioactivity** or half-life. Therefore, the only connection between **UV/EB radiation** and **radioactivity** is purely linguistic. Both **radiation** and **radioactivity** use the root radi- to describe radial propagation of energy by quantum particles or **electromagnetic waves**.

We hope that this clarifies more misconceptions than it may cause, for as Alfred North Whitehead once said, "All truths are only half-truths." This is true because the human mind cannot understand or accept whole truths. We all function on half-truths that we can understand. We can act intelligently only when we have the capability to understand what we are doing.

APPENDIX B

EXAMPLES OF UV/EB COATING AND INK USE

ABRASIVES

Abrasives can be permanently bonded instantly. This eliminates an energy-intensive 8 hour or longer curing that is required for conventional evaporative **coatings** under controlled temperature and ventilation. It also eliminates storage of a day's production under these controlled conditions. **UV**-cured abrasives are instantly ready for use.

DENTISTRY

Dental fillings are another application area. After preparing a tooth, a suitably sized lump of **oligomers**, **photoinitiators**, pigments and fillers is mixed and inserted into a clean dry hole in the tooth. After insertion and molding, an intense **UV** light source (with readily apparent visible light) is directed at it by a wand. In about a minute the **UV** and visible light cures the filling and the person can use their teeth immediately after finishing operations are completed. While this seems slow, it is a much faster cure than silver amalgam fillings. The use of a **radiation**-cured dental filling has an additional benefit in that it avoids ingestion of mercury from silver amalgam fillings.

FIBER REINFORCED PLASTICS

Coatings have also been used as the cement to hold fibers or particles together. These fiber-reinforced-**polymer** items are used to construct **3D** objects. Penetration of **EB radiation** becomes a significant factor when **coating** depth is over 1 centimeter. These thick applications have been cured by **EB** either in a vacuum chamber or with a **cationic photoinitiator**. In these types of applications, **coatings** are not limited to a surface, but also may be found on interfaces at any depth within the object.

FOOD PACKAGING / MENUS

Ten years ago strong odors associated with some **monomers** and **photoinitiators** precluded their use with foods and perfumes. This has been overcome to a large extent, by purification to eliminate malodorous impurities, using a less odiferous **photoinitiator**, or using other alternatives to odiferous additives, **monomers**, or **oligomers**. These deodorized materials have made both printing and overprint **coatings** suitable for packages for fine perfumes, chocolates, and food, and even for restaurant menus.²³

MAGNETIC MEDIA

Printing of magnetic media by orienting magnetic particles of a **coating** to lock magnetic domains of particles in a preferred position before **EB**-curing has benefitted the high density floppy disk and tape manufacturing industry. **EB**-curing also allows a more durable surface after bonding. Such **coatings** must be applied in a clean room to control **coating** thickness, insure surface smoothness, and to eliminate dust particles. **EB**-curing allows these needs to be easily met.

MICROELECTRONICS

In the microelectronics industry, **electron beams** have been focused and used to trace circuits on coated **substrates**. Alternatively, **UV** has been used to cure a **coating** through a mask. The **coating** (which is referred to as a photoresist) is cured by the focused **EB** along a path where a **substrate** must be protected from the next step in the process. The **coating** is then “developed” by washing any uncured **resin** away with a **solvent**. This leaves uncured parts of the **substrate** unprotected from reagents used to subsequently etch, deposit a dopant (an atomic species that changes the electronic properties of the **substrate**), or deposit metal conductors. It has been found that for very sharp demarcation of edges of a cured **polymer**, a **coating** thickness has to be no thicker than the width of a line on the microelectronics. Microelectronics now uses lines only 0.18 microns wide. This thin layer of **monomer** is applied by diluting or heating the **coating** to reduce viscosity and then spreading it by high-speed spinning of the **substrate** to centrifuge most of the **coating** away. The **substrate** is usually a sliced and polished section of a purified silicon ingot (called a boule) about 4 inches in diameter.

To be able to use **UV**, the wavelength must be shorter. This is referred to as extreme **UV**. This process requires a thin film that can be either **UV**-cured through a mask, or **EB**-cured along a path. For a **UV** cure, **UV radiant energy** must be at a wavelength that the **photoinitiator** can adsorb and that delineates a clear image (edge), even if the path is obstructed. For an **EB** cure, **EB radiant energy** must be focused to a spot no larger than the finest line that must be produced. This produces an **EB** that cures the thin film instantly at low voltage.

After the cured **coating** has performed its function of providing a mask for reagents, the cured **polymer** is stripped off and another thin **coating** of photoresist is applied before the next step of the process is performed. This is repeated several times when an integrated circuit is created. Integrated circuits are used as central processor units, as memory, as programmable gate arrays, and as various logic components that are used on circuit boards to make digital circuits.

On printed circuit boards, features such as solder masks, notations, encapsulates and conformal **coatings** all use a thicker **UV/EB**-curable **coating** than that used in making integrated circuits. Although curing of **UV/EB coatings** on circuit boards is fast, it is not as rapid as **EB**-curing for microelectronics (extremely rapid). However, the time required for curing microelectronics is per unit length along the track within the mask, while curing for circuit board **coatings** occurs all at once.

OPTICAL FIBERS

3D techniques have been applied to cure **coatings** on optical fibers. The inner **coating** on optical fibers has a low index of refraction that redirects light (the signal) back into the fiber. An overcoat for these fibers provides abrasion resistance and adds to mechanical strength. An optically absorbent final **coating** prevents undesirable “crosstalk” between fibers. Without these **radiation**-cured **coatings**, long distance optical fiber communications could not have come into existence.

PRESSURE SENSITIVE ADHESIVES

Use of **UV/EB coatings** with pressure sensitive **adhesives** is seldom advertised. Pressure sensitive **adhesives** are used to bond metallization to wrappings, for tapes and labels, and to laminate. Advantages include: (1) use of single-component materials that can be dispensed with automated equipment; (2) long open time without losing volatile ingredients; (3) fast cures after dispensing; (4) low energy requirement for curing; and (5) ability to be used on temperature sensitive **substrates** such as paper and plastic films.

PRINTING

UV/EB coatings had their start in printing and many terms from printing are generically used - such as **web** that refers to a continuous flexible **substrate** that is unrolled, passes through the printing press and drying ovens, and is then re-rolled. **Radiation**-cured printing **inks** are used for lithographic, rotogravure, screen, and flexographic printing.^{3,4} All of these types of printing are in a state of rapid evolution with former distinctions between them becoming blurred. As a result, any generalization may have already become obsolete. For example, flexography has historically used a low viscosity **ink**. While **UV/EB**-cured **inks** are more viscous than the traditional flexographic **inks**, **UV/EB**-cured **inks** are used in flexography anyway. **UV/EB radiation**-cured **inks** allow printing presses to have **web** speeds of 400-1000 feet per minute.

The advent of **ultraviolet** lasers has allowed **UV**-curing of photopolymer printing plates without need for a negative transparency. The **ultraviolet** laser is computer controlled, and can be used to make any number of identical plates at any number of sites. These plates can then make identical impressions on any number of presses. This eliminates the need for printing plates that can make a million impressions and adds to the capacity to reproduce images.

RELEASE COATINGS

Release **coatings** are usually silicones applied to plastic or paper. Silicone **resin** producers worked with equipment producers and flexible packaging printers to produce desired **UV/EB radiation**-cured release **coatings**. Labels and double-sided tapes with pressure sensitive **adhesive coatings** are normally placed on a release **coating** until they are applied.

SPRAY COATING

UV/EB-cured paints are suitable for spray-**coating** and can realize up to 99% overall effectiveness in applying a **coating** to a **substrate** when capture and reuse of **overspray** are considered. **Coatings** have been applied to materials that are porous (such as wood or ceramics) or impervious (such as plastics or metal). This overall effectiveness is significantly greater than that for conventional **coatings** because captured **UV/EB** droplets can be reused. This can be done because **UV coatings** can have essentially zero **VOC** content and do not cure unless exposed to an appropriate **radiation** source.

VINYL FLOORING

Vinyl floor **coatings** are second only to paper **coatings** in use of **UV/EB**-cured **coatings**. Premium grade no-wax vinyl flooring uses a **UV/EB** topcoat consisting of two layers. The first layer is a barrier coat to seal the vinyl and provide better adhesion for the final layer. The final layer is an abrasion resistant **coating** to improve wear characteristics.

WOOD PRODUCTS

UV wood product **coatings** have been used for a long time. They were used first to coat panels with polyester **resins**. Acrylic and urethane-acrylic **coatings** have since been used on panels for greater durability. Further developments have included **3D** cure of sealers and primers for wood furniture. **UV radiation** curing of topcoats for fine furniture allows a shorter cure time (a few seconds) with fewer dust flaws in the wet surface.

The example given for emissions in the 1991 reference is now outdated. The use of **VOC** as thinners in furniture **coatings** is now obsolete. In 1999, wood furniture used water thinned **UV**-cured **coatings**, **monomer** thinned **UV**-cured **coatings**, heat and **reactive diluents** when temperature alone could not sufficiently control viscosity.

APPENDIX C

EMISSION MEASUREMENT TECHNICAL INFORMATION CENTER NSPS TEST METHOD

(EMTIC -24, 9/11/95)

Method 24 - Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. APPLICABLE STANDARD METHODS

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475-60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

2.2 ASTM D 2369-81, Standard Test Method for Volatile Content of Coatings.

2.3 ASTM D 3792-79, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

2.4 ASTM D 4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

2.5 ASTM 4457-85 Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (incorporated by reference--see §60.17).

2.6 ASTM D 5403-93 Standard Test Methods for Volatile Content of Radiation Curable Materials (incorporated by reference--see §60.17).

3. PROCEDURE

3.1 Multicomponent Coatings. Multicomponent coatings are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating. To determine the total volatile content, water content, and density of multicomponent coatings, follow the procedures in section 3.8.

3.2 Non Thin-film Ultraviolet Radiation-cured Coating. To determine volatile content of non thin-film ultraviolet radiation-cured (UV radiation-cured) coatings, follow the procedures in Section 3.9. Determine water content, density and solids content of the UV-cured coatings according to Sections 3.4, 3.5, and 3.6, respectively. The UV-cured coatings are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light. To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D \quad \text{Eq.}$$

where:

A = Area of substrate, in², cm².

C = Amount of coating or ink added to the substrate, g.

D = Density of coating or ink, g/in³ (g/cm³)

F = Manufacturer's recommended film thickness, in (cm).

If C is less than 0.2 g and A is greater than or equal to 35 in² (225 cm²) then the coating or ink is considered a thin-film UV radiation-cured coating for determining applicability of ASTM D 5403-93. NOTE: As noted in Section 1.4 of ASTM D 5403-93, this method may not be applicable to radiation curable materials wherein the volatile material is water. For all other coatings not covered by Sections 3.1 or 3.2 analyze as follows:

3.3 Volatile Matter Content. Use the procedure in ASTM D 2369-81 to determine the volatile matter content (may include water) of the coating.

3.3.1 Record the following information:

W₁ = Weight of dish and sample before heating, g.

W₂ = Weight of dish and sample after heating, g.

W₃ = Sample weight, g.

3.3.2 Run analyses in pairs (duplicate sets) for each coating until the criterion in Section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = (W_1 - W_2)/W_3 \quad \text{Eq. 24-2}$$

Record the arithmetic average (\bar{W}_v).

3.4 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792-79 or ASTM D 4017-81. A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in Section 4.3 is met. Record the arithmetic average (W_w).

3.5 Coating Density. Determine the density (D_c , kg/liter) of the surface coating using the procedure in ASTM D 1475-60. Run duplicate sets of determinations for each coating until the criterion in Section 4.3 is met. Record the arithmetic average (D_c).

3.6 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

3.7 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457-85 (incorporated by reference--see §60.17). Run a duplicate set of determinations and record the arithmetic average (W_E).

3.8 To determine the total volatile content, water content, and density of multicomponent coatings, use the following procedures:

3.8.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 3.5.

3.8.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density. To determine water content follow

section 3.4. To determine density, follow section 3.5. To determine total volatile content, use the apparatus and reagents described in ASTM D2369-81, sections 3 and 4, respectively (incorporated by reference, and see §60.17) the following procedures:

3.8.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ± 1 ml of suitable solvent as specified in ASTM D2369-81 to the weighing dish. Using a syringe as specified in ASTM D2369-81, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 ± 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ± 0.1 g.

NOTE: If the volatile content determined pursuant to section 5 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven dried at $110 \pm 5^\circ\text{C}$, for 1 hour.

3.8.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at $110 \pm 5^\circ\text{C}$. Caution -- provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

3.8.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

3.8.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 4.3 is met. Calculate W_v following Equation 24-2 and record the arithmetic average.

3.9 UV-cured Coating's Volatile Matter Content. Use the procedure in ASTM D 5403-93 (incorporated by reference--see §60.17) to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403-93 is required.

4. DATA VALIDATION PROCEDURE

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for

the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of water-borne coatings as the weight percent water increases, measured parameters for water-borne coatings are

modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-Laboratory
Volatile matter content, W_v	1.5% $\underline{W_v}$	4.7% $\underline{W_v}$
Water content, W_w	2.9% $\underline{W_w}$	7.5% $\underline{W_w}$
Density, D_c	001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For W_v and W_w , run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, MD-13, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows: To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c , use the lower confidence limits, and for W_w , use the upper confidence limit. Because V_s is calculated, there is no adjustment for this parameter.

5. CALCULATIONS

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \quad \text{Eq. 24-3}$$

where: W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \quad \text{Eq. 24-4}$$

5.2 Weight Fraction Solids.

$$W_s = 1 - W_v. \quad \text{Eq. 24-5}$$

where: W_s = Weight solids, g/g.

APPENDIX D

Definition of Volatile Organic Compounds (VOC)

As of 2/25/99

40 CFR 51.100(s) - Definition - **Volatile organic compounds (VOC)**

"Volatile organic compounds (VOC)" means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

(1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity:

- methane
- ethane
- methylene chloride (dichloromethane)
- 1,1,1-trichloroethane (methyl chloroform)
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
- trichlorofluoromethane (CFC-11)
- dichlorodifluoromethane (CFC-12)
- chlorodifluoromethane (HCFC-22)
- trifluoromethane (HFC-23)
- 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114)
- chloropentafluoroethane (CFC-115)
- 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123)
- 1,1,1,2-tetrafluoroethane (HFC-134a)
- 1,1-dichloro 1-fluoroethane (HCFC-141b)
- 1-chloro 1,1-difluoroethane (HCFC-142b)
- 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)
- pentafluoroethane (HFC-125)
- 1,1,2,2-tetrafluoroethane (HFC-134)
- 1,1,1-trifluoroethane (HFC-143a)
- 1,1-difluoroethane (HFC-152a)
- parachlorobenzotrifluoride (PCBTF)
- cyclic, branched, or linear completely methylated siloxanes
- acetone
- perchloroethylene (tetrachloroethylene)
- 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca)
- 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb)
- 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43-10mee)
- difluoromethane (HFC-32)
- ethylfluoride (HFC-161)
- 1,1,1,3,3,3-hexafluoropropane (HFC-236fa)

- 1,1,2,2,3-pentafluoropropane (HFC-245ca)
- 1,1,2,3,3-pentafluoropropane (HFC-245ea)
- 1,1,1,2,3-pentafluoropropane (HFC-245eb)
- 1,1,1,3,3-pentafluoropropane (HFC-245fa)
- 1,1,1,2,3,3-hexafluoropropane (HFC-236ea)
- 1,1,1,3,3-pentafluorobutane (HFC-365mfc)
- chlorofluoromethane (HCFC-31)
- 1-chloro-1-fluoroethane (HCFC-151a)
- 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a)
- 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C4F9OCH3)
- 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF3)2CFCF2OCH3)
- 1-ethoxy-1,1,2,2,3,3,3,4,4-nonafluorobutane (C4F9OC2H5)
- 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF3)2CFCF2OC2H5)
- methyl acetate and perfluorocarbon compounds which fall into these classes:
 - (i) cyclic, branched, or linear, completely fluorinated alkanes,
 - (ii) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations,
 - (iii) cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations, and
 - (iv) sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

(2) For purposes of determining compliance with emissions limits, **VOC** will be measured by the test methods in the approved State implementation plan (SIP) or 40 CFR Part 60, Appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibly-reactive compounds may be excluded as **VOC** if the amount of such compounds is accurately quantified, and such exclusion is approved by the enforcement authority.

(3) As a precondition to excluding these compounds as **VOC** or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligibly-reactive compounds in the source's emissions.

(4) For purposes of Federal enforcement for a specific source, the EPA shall use the test methods specified in the applicable EPA-approved SIP, in a permit issued pursuant to a program approved or promulgated under Title V of the Act, or under 40 CFR Part 51, Subpart I or Appendix S, or under 40 CFR Parts 52 or 60. The EPA shall not be bound by any State determination as to appropriate methods for testing or monitoring negligibly-reactive compounds if such determination is not reflected in any of the above provisions.

Note to reader: This has been formatted to make it easier for the user to read.

APPENDIX E

HAZARDOUS AIR POLLUTANTS (HAP)

This appendix contains the original list of **hazardous air pollutants** from the Clean Air Act Amendments of 1990 followed by a list of final and proposed modifications to the list.

HAP LIST FROM THE CLEAN AIR ACT AMENDMENTS OF 1990

<u>CAS Number</u>	<u>Chemical Name</u>
75070	Acetaldehyde
60355	Acetamide
75058	Acetonitrile
98862	Acetophenone
53963	2-Acetylaminofluorene
107028	Acrolein
79061	Acrylamide
79107	Acrylic acid
107131	Acrylonitrile
107051	Allyl chloride
92671	4-Aminobiphenyl
62533	Aniline
90040	o-Anisidine
133221	Asbestos
71432	Benzene (including benzene from gasoline)
92875	Benzidine
98077	Benzotrichloride
100447	Benzyl chloride
92524	Biphenyl
117817	Bis(2-ethylhexyl)phthalate (DEHP)
542881	Bis(chloromethyl)ether
75252	Bromoform
106990	1,3-Butadiene
156627	Calcium cyanamide
105602	Caprolactam (See Modification)
133062	Captan
63252	Carbaryl
75150	Carbon disulfide
56235	Carbon tetrachloride
463581	Carbonyl sulfide

<u>CAS Number</u>	<u>Chemical Name</u>
120809	Catechol
133904	Chloramben
57749	Chlordane
7782505	Chlorine
79118	Chloroacetic acid
532274	2-Chloroacetophenone
108907	Chlorobenzene
510156	Chlorobenzilate
67663	Chloroform
107302	Chloromethyl methyl ether
126998	Chloroprene
1319773	Cresols/Cresylic acid (isomers and mixture)
95487	o-Cresol
108394	m-Cresol
106445	p-Cresol
98828	Cumene
94757	2,4-D, salts and esters
3547044	DDE (See technical note)
334883	Diazomethane
132649	Dibenzofurans (See technical note)
96128	1,2-Dibromo-3-chloropropane
84742	Dibutylphthalate
106467	1,4-Dichlorobenzene(p)
91941	3,3-Dichlorobenzidine (See technical note)
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)
542756	1,3-Dichloropropene
62737	Dichlorvos
111422	Diethanolamine
121697	N,N-Diethyl aniline (N,N-Dimethylaniline) (See technical note)
64675	Diethyl sulfate
119904	3,3-Dimethoxybenzidine (See technical note)
60117	Dimethyl aminoazobenzene
119937	3,3'-Dimethyl benzidine (See technical note)
79447	Dimethyl carbamoyl chloride (See technical note)
68122	Dimethyl formamide

<u>CAS Number</u>	<u>Chemical Name</u>
57147	1,1-Dimethyl hydrazine (See technical note)
131113	Dimethyl phthalate
77781	Dimethyl sulfate
534521	4,6-Dinitro-o-cresol, and salts
51285	2,4-Dinitrophenol
121142	2,4-Dinitrotoluene
123911	1,4-Dioxane (1,4-Diethyleneoxide)
122667	1,2-Diphenylhydrazine
106898	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
106887	1,2-Epoxybutane
140885	Ethyl acrylate
100414	Ethyl benzene (See technical note)
51796	Ethyl carbamate (Urethane)
75003	Ethyl chloride (Chloroethane)
106934	Ethylene dibromide (Dibromoethane)
107062	Ethylene dichloride (1,2-Dichloroethane)
107211	Ethylene glycol
151564	Ethylene imine (Aziridine)
75218	Ethylene oxide
96457	Ethylene thiourea
75343	Ethylidene dichloride (1,1-Dichloroethane)
50000	Formaldehyde
76448	Heptachlor
118741	Hexachlorobenzene
87683	Hexachlorobutadiene
77474	Hexachlorocyclopentadiene
67721	Hexachloroethane
822060	Hexamethylene-1,6-diisocyanate
680319	Hexamethylphosphoramide
110543	Hexane
302012	Hydrazine
7647010	Hydrochloric acid (See technical note)
7664393	Hydrogen fluoride (Hydrofluoric acid)
7783064	Hydrogen sulfide (See Modification)
123319	Hydroquinone

<u>CAS Number</u>	<u>Chemical Name</u>
78591	Isophorone
58899	Lindane (all isomers)
108316	Maleic anhydride
67561	Methanol
72435	Methoxychlor
74839	Methyl bromide (Bromomethane)
74873	Methyl chloride (Chloromethane)
71556	Methyl chloroform (1,1,1-Trichloroethane)
78933	Methyl ethyl ketone (2-Butanone)
60344	Methyl hydrazine
74884	Methyl iodide (Iodomethane)
108101	Methyl isobutyl ketone (Hexone)
624839	Methyl isocyanate
80626	Methyl methacrylate
1634044	Methyl tert butyl ether(See technical note)
101144	4,4-Methylene bis(2-chloroaniline)(See technical note)
75092	Methylene chloride (Dichloromethane)
101688	Methylene diphenyl diisocyanate (MDI)
101779	4,4'-Methylenedianiline
91203	Naphthalene
98953	Nitrobenzene
92933	4-Nitrobiphenyl
100027	4-Nitrophenol
79469	2-Nitropropane
684935	N-Nitroso-N-methylurea
62759	N-Nitrosodimethylamine
59892	N-Nitrosomorpholine
56382	Parathion
82688	Pentachloronitrobenzene (Quintobenzene)
87865	Pentachlorophenol
108952	Phenol
106503	p-Phenylenediamine
75445	Phosgene
7803512	Phosphine
7723140	Phosphorus (See technical note)

<u>CAS Number</u>	<u>Chemical Name</u>
85449	Phthalic anhydride
1336363	Polychlorinated biphenyls (Aroclors)
1120714	1,3-Propane sultone
57578	beta-Propiolactone
123386	Propionaldehyde
114261	Propoxur (Baygon)
78875	Propylene dichloride (1,2-Dichloropropane)
75569	Propylene oxide
75558	1,2-Propylenimine (2-Methyl aziridine)
91225	Quinoline
106514	Quinone
100425	Styrene
96093	Styrene oxide
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethylene (Perchloroethylene)
7550450	Titanium tetrachloride
108883	Toluene
95807	2,4-Toluene diamine
584849	2,4-Toluene diisocyanate
95534	o-Toluidine
8001352	Toxaphene (chlorinated camphene)
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethylene
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
121448	Triethylamine
1582098	Trifluralin
540841	2,2,4-Trimethylpentane
108054	Vinyl acetate
593602	Vinyl bromide
75014	Vinyl chloride
75354	Vinylidene chloride (1,1-Dichloroethylene)
1330207	Xylenes (isomers and mixture)

<u>CAS Number</u>	<u>Chemical Name</u>
95476	o-Xylenes (See technical note)
108383	m-Xylenes (See technical note)
10642	p-Xylenes (See technical note)
	Antimony Compounds
	Arsenic Compounds (inorganic including arsine)
	Beryllium Compounds
	Cadmium Compounds
	Chromium Compounds
	Cobalt Compounds
	Coke Oven Emissions
	Cyanide Compounds ¹
	Glycol ethers ²
	Lead Compounds (See technical note)
	Manganese Compounds
	Mercury Compounds
	Fine mineral fibers ³ (See technical note)
	Nickel Compounds
	Polycyclic Organic Matter ⁴ (See technical note)
	Radionuclides (including radon) ⁵
	Selenium Compounds

NOTE: For all listings above which contain the word "compounds" and for glycol ethers, the following applies:

Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

1. X'CN where X = H' or any other group where a formal dissociation may occur. For example KCN or Ca(CN)₂

2. Includes mono- and di- ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH₂CH₂)_n-OR'

where

n = 1, 2, or 3

R = alkyl or aryl groups

R' = R, H, or groups which, when removed, yield glycol ethers with the structure:

R-(OCH₂CH)_n-OH. **Polymers** are excluded from the glycol category. (See Modification)

3. Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

4. Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 °C.
5. A type of atom which spontaneously undergoes radioactive decay.

Technical Note: Minor editorial/technical issue - call (919) 541-5347 for details.

Modifications To The 112(b)1 Hazardous Air Pollutants

Authority for modifications:

Section 112 of the Act contains a mandate for EPA to evaluate and control emissions of **hazardous air pollutants**. Section 112(b)(1) includes an initial list of **hazardous air pollutants** that is composed of specific chemical compounds and compound classes to be used to identify source categories for which the EPA will promulgate emissions standards. The listed categories are subject to emission standards subsequently developed under Section 112. The EPA must periodically review the list of **hazardous air pollutants** and, where appropriate, revise this list by rule. In addition, any person may petition EPA under Section 112(b)(3) to modify the list by adding or deleting one or more substances. A petitioner seeking to delete a substance must demonstrate that there are adequate data on the health and environmental effects of the substance to determine that emissions, ambient concentrations, bioaccumulation, or deposition of the substance may not reasonably be anticipated to cause any adverse effects to human health or the environment. To demonstrate the burden of proof, a petitioner must provide a detailed evaluation of the available data concerning the substance's potential adverse health and environmental effects, and estimate the potential exposures through inhalation or other routes resulting from emissions of the substance.

Modifications:

Glycol Ethers - Proposed

On January 12, 1999 (FR64:1780), EPA proposed to modify the definition of glycol ethers to exclude surfactant alcohol ethoxylates and their derivatives (SAED). This proposal was based on EPA's finding that emissions, ambient concentrations, bioaccumulation, or deposition of SAED may not reasonably be anticipated to cause adverse human health or environmental effects. EPA also proposed to make conforming changes in the definition of glycol ethers with respect to the designation of hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The proposal reads as follows:

"The definition of the glycol ethers category of **hazardous air pollutants**, as established by 42 U.S.C. 7412(b)(1) includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol $R-(OCH_2CH_2)_n-OR'$ Where:

n= 1, 2, or 3

R= alkyl C7 or less, or phenyl or alkyl substituted phenyl

R'= H, or alkyl C7 or less, or carboxylic acid ester, sulfate, phosphate, nitrate, or sulfonate."

Methyl Ethyl Ketone(MEK) - Notices of Review

Hazardous Air Pollutant list - Methyl Ethyl Ketone(MEK); receipt of a complete petition to delist Citation: 64 FR 33453; Date: 06/23/99

Caprolactam

On July 19, 1993, EPA received a petition from AlliedSignal, Inc., BASF Corporation, and DSM Chemicals North America, Inc. to delete caprolactam (CAS No. 105-60-2) from the hazardous air pollutant list in Section 112(b)(1), 42 U.S.C., Section 7412(b)(1). A Notice of Receipt was published (58FR45081, August 26, 1993) noting that the data filed were adequate to support decision making. After a comprehensive review of the data submitted, the EPA published a proposal to delist caprolactam (60FR48081, September 18, 1995). In order to help address public concern, on March 13, 1995, EPA executed two detailed agreements with AlliedSignal concerning the Irmo, South Carolina manufacturing facility and another facility located in Chesterfield, Virginia, copies of which are included in the public docket for this rulemaking. AlliedSignal agreed that, if caprolactam was delisted pursuant to the proposal, AlliedSignal would install emissions controls which EPA believed would be equivalent to the controls which would have been required had EPA issued a standard to control these sources under Section 112. The agreed emissions controls are incorporated in federally enforceable operating permits for the affected facilities, and will be in place years earlier than controls would have otherwise been required. In addition, AlliedSignal has agreed to establish a citizen advisory panel concerning the Irmo facility in order to improve communications with the community and to assure that citizens have an ongoing role in implementation of the agreed emission reductions. The public requesting a public hearing. On November 28, 1995, the EPA published a notice of public hearing and an extension of the comment period (60FR58589). After considering all public comments, the EPA published a final rule delisting caprolactam (61FR30816, June 18, 1996).

All information associated with this rule making is located in Docket Number A-94-33 at the Central Docket Section (A-130), Environmental Protection Agency, 401 M St. SW., Washington, D.C. 20460. phone 202-260-7548, fax 202-260-4400, email a-and-r-docket@epamail.epa.gov. The docket includes complete index to all papers filed in this docket, a copy of the original petition, comments submitted, and additional materials supporting the rule. A reasonable fee may be charged for copying. The docket may be inspected in person between 8:00 a.m. and 4:30 p.m. on weekdays at EPA's Central Docket Section, West Tower Lobby, Gallery 1, Waterside Mall, 401 M St., SW, Washington, D.C. 20460.

Hydrogen Sulfide

A clerical error led to the inadvertent addition of hydrogen sulfide to the Section 112(b) list of **Hazardous Air Pollutants**. However, a Joint Resolution to remove hydrogen sulfide from the Section 112(b)(1) list was passed by the Senate on August 1, 1991 (Congressional Record page S11799), and the House of Representatives on November 25, 1991 (Congressional Record pages H11217-H11219). The Joint Resolution was approved by the President on December 4, 1991. Hydrogen Sulfide is included in Section 112(r) and is subject to the accidental release provisions. A study (see citation below) was required under Section 112(n)(5).

Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Natural Gas, EPA-453/R-93-045, (NTIS publication # is PB94-131224, \$36.50 hard copy, \$17.50 microfiche).

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TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing.)</i>		
1. REPORT NO. EPA 456/K-01-001	2.	3. RECIPIENT'S ACCESSION NO.
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	6. PERFORMING ORGANIZATION CODE CATC/ITPID/OAQPS/OAR/EPA	
7. AUTHOR(S) Clean Air Technology Center	8. PERFORMING ORGANIZATION REPORT NO.	
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	11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Final	
	14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES		
16. ABSTRACT <p>This document is a Technical Bulletin which is intended to enlighten the state air pollution authorities about a relatively new technology. This document defines UV/EB coatings, explains why they are important, explains how the technology works, what degree of pollution prevention is afforded, what industries could use UV/EB coatings, and the cost analysis of using UV/EB coatings. It even describes stereolithography, which makes a part out of a coating. UV/EB coatings were previously called UV/EB radiation cured coatings, but "radiation" has been dropped from the name because it is a term that is used too freely. UV/EB cured coatings are used in many applications, and should become useful in more when the results and risks of using them are fully understood. The intent is to make them fully understandable.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field Group
coatings, inks, adhesives, ultraviolet, electron beam, electromagnetic radiation, mercury vapor lamps, organic polymers, free radical polymerization, cationic polymerization, polymer, curing, cure of conventional coatings, visible spectrum, extreme ultraviolet, ozone	Air Pollution Control, Pollution Prevention, Volatile Organic Compounds, Hazardous Air Pollutants	
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