Kirk-Othmer Encyclopedia of Chemical Technology.

RADIATION CURING

The interaction of electromagnetic radiation with organic substrates is of widespread interest and has broad commercial applications. The use of electromagnetic radiation to alter the physical and chemical nature of a material is sometimes termed radiation curing technology. In radiation curing, electromagnetic radiation interacts with organic substrates to develop cross-linked or solvent-insoluble network structures. For example, a preformed thermoplastic polymer that interacts directly with certain types of ionizing (high energy) radiation from a given source of energy can develop into cross-linked or network structures having higher melting points, improved heat resistance, and improved chemical resistance than the original thermoplastic polymer starting materials (Fig. 1; Table 1) (1–3).

Similar types of high energy radiation can be used to cross-link (cure) organic coatings, providing that the liquid coating composition contains reactive vinyl-unsaturated components such as allyl, acrylate, methacrylate, styrene, and fumarate reactive groups (4–7). Radiation curing technology involves consideration of at least four main variables: type of radiation source; organic substrate to be irradiated; kinetics and mechanisms of radiation energy–organic substrate interactions; and final chemical, physical, and mechanical properties associated with the formation of three-dimensional (cured) network structures.

1. Radiation and Electromagnetic Radiation Sources

Radiation curing, as applied to the cross-linking of polymers or coating materials, involves the full spectrum of electromagnetic radiation energies to effect chemical reactions. These forms of radiation energy include ionizing radiation, ie, α-, β-particles and γ-rays from radioactive nuclei; x-rays; high energy electrons; and nonionizing radiation such as are associated with uv, visible, ir, microwave, and radio-frequency wavelengths of energy (Table 2) (8–10).

One of the most common sources of α-, β-, and γ-rays is radioactive nuclei, such as those listed in Table 3. The only significant ionizing radiation having limited commercial polymer-coating curing applications is the γ-ray produced from either ^{60}Co or ^{137}Cs radioactive nuclei. Detailed descriptions of these sources, eg, energies, cost of operation, shielding requirements, comparisons between ^{60}Co and ^{137}Cs efficiencies, and reactor geometries, are available (8, 11–13) (see Radioisotopes).

X-rays can be produced through deceleration of high speed electrons through the electric field of an atomic nucleus. Various types of accelerator equipment capable of producing x-rays are listed in Table 4. High voltage electron accelerators have a distinct advantage over γ-ray and certain types of x-ray processing equipment. High energy electrons produced by machine acceleration, in comparison with radioisotopes, can be applied easily to industrial processes for the following reasons: easy on–off switching capability; less shielding is required than with gamma radiation; accelerator beams are directional and less penetrating than γ- or x-rays; and electron radiation provides high dose rates, ie, maximum penetration per unit density of material, and is well suited for on-line, high speed processing applications.

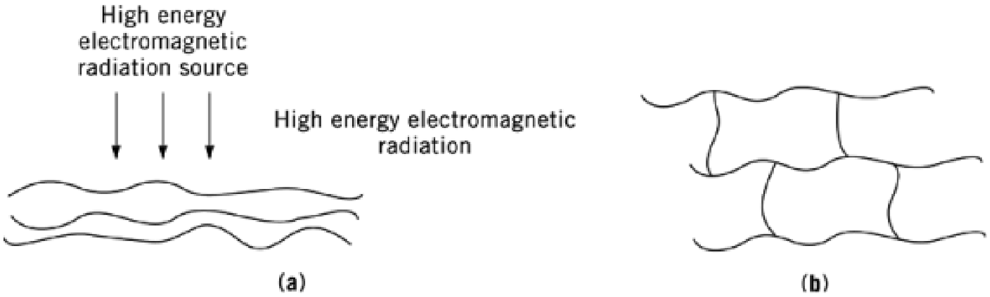


Fig. 1. (**a**) Interaction of high energy electromagnetic radiation with a preformed thermoplastic polymer to develop (**b**) cross-linked network polymer structures.

Table 1. Comparison of Physical Properties for Conventional 105°C PVC and Irradiated PVC Wire Compounds[a]

	Property values	
Physical property	Conventional 105°C PVC	Irradiated PVC
tensile strength, MPa[b]	20.7	20.7
elongation, %	250	200
solder iron resistance, time to fail at 349°C, 0.68-kg load, s	<1	>300
insulation resistance, Ω/30 m	1000	1000
cut-through resistance, time to cut through at 105°C, 0.125-mm chisel, s	<5	>600
heat resistance, % retention of elongation after 168 h at 136°C	50	75

[a] Ref. 3.
[b] To convert MPa to psi, multiply by 145.

Table 2. Electromagnetic Spectrum[a]

Types of radiation	Wavelengths, nm	Frequency, Hz	Energy, eV
gamma ray	$10^{-4} - 10^{-2}$	10^{19}–10^{22}	10^{5}–10^{8}
electron beam	$10^{-3} - 10^{-1}$	10^{18}–10^{21}	10^{4}–10^{7}
x-ray	$10^{-2} - 10$	10^{16}–10^{19}	10^{2}–10^{5}
ultraviolet	10–400	10^{15}–10^{16}	5–10^{2}
visible	400–750	10^{15}	1–5
infrared	750–10^{5}	10^{12}–10^{14}	$10^{-2} - 1$
microwave	$>10^{6}$	10^{11}–10^{12}	$<10^{-2}$
radio frequency	$>10^{6}$	$<10^{11}$	$<10^{-2}$

[a] Refs. 8 and 9.

Commercially available high or low energy electron-processing equipment includes dynamitron, dynacote, insulating-core transformers, linear accelerators, Van de Graaf accelerator, pelletron, laddertron, and planar cathodes (16). Manufacturers of high voltage electron-accelerator equipment are High Voltage Engineering Corporation (Burlington, Massachusetts); Radiation Dynamics, Inc. (Edgewood, New York); Energy Science, Inc. (Woburn, Massachusetts); and Radiation Polymer Company (RPC) (Hayward, California). The two most common high energy electron accelerators in use in the 1990s are the scanned beam configuration (Radiation Dynamics) and the linear or planar cathode system (Energy Sciences and RPC).

Electromagnetic radiation, ie, from photons in the uv and visible ranges, can also produce chemical changes, but these energies do not cause direct ionization of organic substrates. Chemical reaction depends on the ability of the organic substrate or photoactive compounds to absorb light energy and to undergo

Table 3. Radioactive Nuclei[a]

Isotopes	Half-life	Type of radiation
polonium-210	138 d	α,γ-rays
radium-226	1620 yr	α,γ-rays
cesium-137	30 yr	β,γ-rays
cobalt-60	5.27 yr	β,γ-rays
strontium-90	28 yr	β-rays

[a] Ref. 11.

Table 4. X-Ray Processing Equipment[a]

Accelerator	Energy, MeV
x-ray machine	0.05–0.3
resonant transformer	0.1–3.5
Van de Graaf accelerator	1–5
betatron	10–300
linear electron accelerator	3–630

[a] Refs. (11, 14), and 15.

photophysical processes involving electronically excited states and photochemical processes, which ultimately result in the formation of reactive intermediates (free radical or acid catalysts) that cause the organic substrate cross-linking reactions to occur.

Ultraviolet light sources are based on the mercury vapor arc. The mercury is enclosed in a quartz tube and a potential is applied to electrodes at either end of the tube. The electrodes can be of iron, tungsten, or other metals and the pressure in a mercury vapor lamp may range from less than 0.1 to $>$1 MPa ($<$1 to $>$10 atm). As the mercury pressure and lamp operating temperatures are increased, the radiation becomes more intense and the width of the emission lines increases (17).

Visible light sources can be obtained from high pressure mercury arcs by addition of rare gases or metal halides, which increase the number of emission lines in the 350–600-nm region of the spectrum. Fluorescent lamps, tungsten halide lamps, and visible lasers are also used for light-induced photochemical reactions as applied to the curing of polymers and coating technologies (18).

Infrared radiation ($\lambda = (0.7 - 400\ \mu\text{m})$ has been used to fabricate plastics and to cure coating systems for a wide variety of commercial applications. In these applications, either gas fuel or electricity generates the infrared radiation (9, 19–21). Gas-fired infrared-generating systems include radiant tube burners, surface combination burners, and direct-fired refractory burners. Electrically powered infrared-generating systems are short-wave emitter lamps, radiant metallic rods, and ceramic, quartz, or glass tubes (see Infrared technology).

The energy density of microwaves is proportional to the square of the electrical field intensity at a given point of reference. Microwaves can generate thermal energy through resistive losses in a conductor, magnetic losses in magnetic materials, and dielectric losses in materials having high dielectric constants (19). Microwave heating equipment consists of the following five main elements: a power supply, which converts 440 V, three-phase, 60 Hz to 1–20 kV dc; a high frequency generating system (magnetron or klystron tube circuits); a high frequency transmission system (microwave waveguides); a control system; and work application fixtures.

Radio-frequency energies (4–5 MHz (1–100 W)) initiate glow discharge, ie, plasma polymerization reactions for a wide variety of organic starting materials. These types of energetic gas-phase reactions produce thin cross-linked films that have a broad range of useful physical properties (22, 23). Typical plasma or glow discharge monomer polymerization or polymer modification reaction equipment consists of the following components: a radio-frequency power source, a standing-wave ratio bridge, a matching network, inductive coupling or capacitor electrodes, and a vacuum system (see Microwave technology; Plasma technology).

2. Mechanisms of Radiation Energy–Organic Substrate Interaction

High energy interaction with organic substrates produces excited states which undergo secondary reactions, eg, electron capture, charge neutralization, intermolecular and intramolecular energy-transfer processes, ion formation, and molecular dissociation to produce free-radical intermediate species. The resulting chemical reactions are caused by the excited species and the formation of reactive intermediates (11). Ionizing radiation can produce excited molecules and secondary reactions through the following direct interaction processes:

$$\begin{aligned}
&\text{A:B} \overset{\gamma\text{-ray, x-ray, or high energy electrons}}{\rightsquigarrow} (\text{A:B})^{*} \text{ (excited state)}\\
&(\text{A:B})^{*} \rightsquigarrow (\text{A}\cdot\text{B})^{\dot{+}} \text{ (radical - ion)} + e^{-} \text{ (electron ejection)}\\
&(\text{A}\cdot\text{B})^{\dot{+}} \rightsquigarrow \text{A}^{+}\text{(ion)} + \text{B}\cdot\text{(free radical)}\\
&(\text{A:B})^{*} + \text{C:D} \longrightarrow \text{A:B} + (\text{C:D})^{*} \text{ (energy transfer)}\\
&(\text{A}\cdot\text{B})^{+} + e^{-} \longrightarrow (\text{A:B})^{*} \text{ (electron capture)}\\
&\text{C:D} + e^{-} \longrightarrow (\text{C:D})^{-} \text{ (electron capture)}\\
&(\text{A}\cdot\text{B})^{+} + (\text{C:D})^{-} \longrightarrow (\text{A:B})^{*} + (\text{C:D})^{*} \text{ (charge neutralization)}\\
&(\text{A:B})^{*} \longrightarrow \text{A}\cdot + \text{B}\cdot \text{ (molecular dissociation)}
\end{aligned}$$

In the case of photochemical reactions, light energy must be absorbed by the system so that excited states of the molecule can form and subsequently produce free-radical intermediates (24, 25) (see Photochemical technology).

$$\text{A:B} \xrightarrow[\text{uv or visible light energies}]{h\upsilon \text{ (photons)}} (\text{A:B})^{*} \text{ (exicted states)}$$

$$(\text{A} : \text{B})^{*} \longrightarrow \text{A} + \text{B} \text{ (free} - \text{radical intermediates)}$$

It is also possible to use special photoactive catalysts that absorb light energy and produce cation or acid-reactive intermediates.

$$\text{photoactive catalyst} \xrightarrow{h\upsilon \text{ (photons)}} [\text{excited states}]^{*}$$

$$[\text{excited states}]^{*} \longrightarrow \text{acids or cations}$$

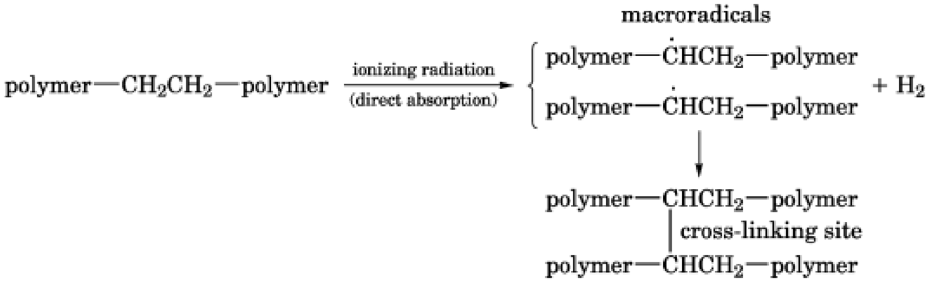
The difference between excited states produced by ionizing radiation and those produced photochemically is that an incident photon does not have sufficient energy to eject an electron completely from the molecule but only displaces it into a new orbital farther from the nucleus. Ionizing radiation produces the same types of excited states as photochemical processes, but ionizing radiation also produces higher excited states, ie, of more intrinsic energy, which cannot be formed directly by absorption of light energies (11, 26). Energies emitted from an infrared source are transmitted directly to the surface of an organic substrate where they are absorbed, reflected, and/or transmitted, thereby causing vibrational and rotational molecular processes, which are subsequentially converted into heat (19, 27, 28).

Microwave curing of organic substrates involves dielectric loss of energy, which results in heat formation. In an oscillating electric field, organic substrates having high dipole moments, ie, high dielectric constants and high tan δ power factors, align, rotate, and realign, and these changes cause internal molecular friction and conversion of the electromagnetic energy into thermal energy. Rapidly oscillating electric fields cause a greater rate of conversion to heat than do lower frequency electromagnetic waves. Because microwave fields vary from 1–10 GHz, the rate of electromagnetic energy conversion to heat energy is significant (19).

Microwave or radio frequencies above 1 MHz that are applied to a gas under low pressure produce high energy electrons, which can interact with organic substrates in the vapor and solid state to produce a wide variety of reactive intermediate species: cations, anions, excited states, radicals, and ion radicals. These intermediates can combine or react with other substrates to form cross-linked polymer surfaces and cross-linked coatings or films (22, 23, 29).

3. Curing Polymers with γ-Rays, X-Rays, and High Energy Electrons

Radiation curing of preformed polymers using ionizing radiation processing equipment can result in two types of chemical change that are associated with cross-linking and degradation reaction mechanisms. Cross-linking reaction mechanisms on preformed polymer substrates usually involve removal of hydrogen atoms to form a macroradical intermediate. These macroradical intermediates can then couple to form a single molecule. This coupling results in an increase in the original average molecular weight of the starting polymer.



If irradiation continues, the original polymer substrate is transformed into one gigantic molecule of infinite molecular weight having lower solvent solubility, higher melting point, and improved physical properties over the original material (30). Enhancement of cross-linking can be facilitated through the use of multifunctional vinyl monomers or oligomers, $(CH_2{=}CH)_nR$, (meth)acrylates, allyl methacrylate, divinylbenzene, etc, which copolymerize and propagate much more rapidly than in a direct coupling reaction to form greater amounts of gel or cross-linked material at lower dose rates and shorter reaction times (31).

$$\text{polymer} + (CH_2{=}CH)_nR \xrightarrow[\text{radiation}]{\text{ionizing}} \text{rapid gel formation}$$

Radiation-induced degradation reactions are in direct opposition to cross-linking or curing processes, in that the average molecular weight of the preformed polymer decreases because of chain scission and without any subsequent

$$\underset{\text{(high molecular weight)}}{\text{polymer—polymer}} \xrightarrow{\text{ionizing radiation}} \underset{\text{(low molecular weight)}}{\text{polymer}} + \underset{\text{(low molecular weight)}}{\text{polymer}}$$

Examples of typical radiation curable polymer systems, experimental conditions, and applications are listed in Table 5.

Table 5. Ionizing Radiation Interactions with Polymeric Substrates[a].

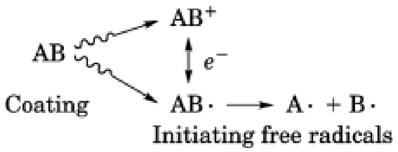
Radiation source	Polymer	Results	Reference
^{60}Co	polyethylene	6% gel content at 12 kGy	(31, 34)
	polyethylene plus 0.5 wt % ethylene glycol diacrylate	30% gel content at 12 kGy	34
	polyethylene plus 4 wt % allyl methacrylate	improved heat stability and tensile strength over polyethylene without added cross-linking monomer	(31, 34)
	polypropylene	onset of gel formation requires 500 kGy with large amounts of degradation products	(31, 35)
	polypropylene plus allyl acrylate	70% gel content at 50 kGy	(31, 35)
electron beam	poly(vinyl chloride)	electrical applications	(36, 37)
	cross-linked silicone rubber	cable termination cover and other electrical applications	(15, 38)
	polyester	degradation and cross-linking reactions are correlated with chemical structure of the polyester	32
	polyethylene, neoprene, and silicone rubbers	heat-shrinkable articles for film packaging and electrical connector applications	(39, 40)
electron beam and ^{60}Co	polyethylene	10–800 kGy, 6.4-mm thick slabs; electrical applications	34
	poly(vinylidene fluoride)s, polyimides, ethylene–alkyl acrylate copolymers, nylons, and natural polymers	wide range of applications	(8, 15)
x-rays	polysulfones	photoresist technologies	41

[a] 1 Gy = 100 rad (10 kGy = 1 Mrad)

4. Curing of Coatings with Electron Beams, γ-Ray, X-Ray, and Planar Cathodes

In conventional gas oven and other heat energy sources associated with the thermal curing of coatings, a mixture of polymers, cross-linking oligomers, catalysts, additives, pigments, and fillers are dissolved or dispersed in organic or water-based solvents to form a coating system. The coating is applied to a substrate and the solvents are thermally removed. The coating cross-links into a three-dimensional network by an energy-rich chemistry, which requires a high degree of thermal energy to convert the polymers into those having useful commercial properties. Much of the energy is absorbed by the substrate before heat reaches the polymers to initiate the curing chemistry (Fig. 2) (4, 5, 42).

High energy electron-curable coatings generally consist of multifunctional acrylate or methacrylate unsaturated polymers. They differ from conventional coatings in that the solvents for the polymers are high boiling, usually nonvolatile, and 100% coreactive with themselves and with other organic components in the film. The curing process for these coatings is a free-radical chain reaction. Ionizing radiation from the processing equipment is absorbed directly in the coating and generates the free radicals that initiate the curing process.



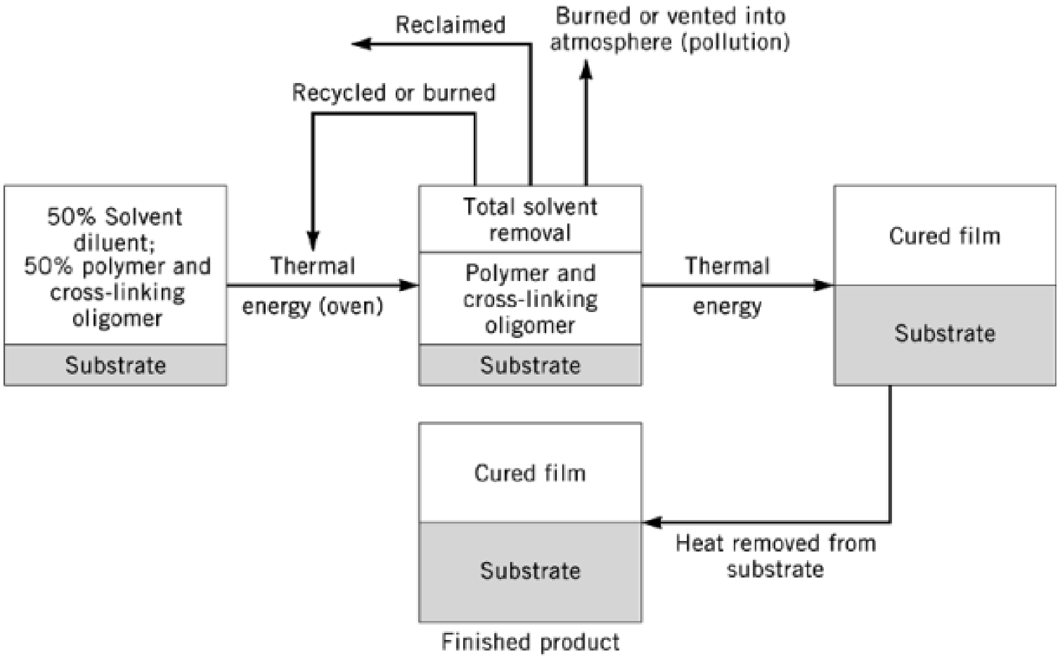
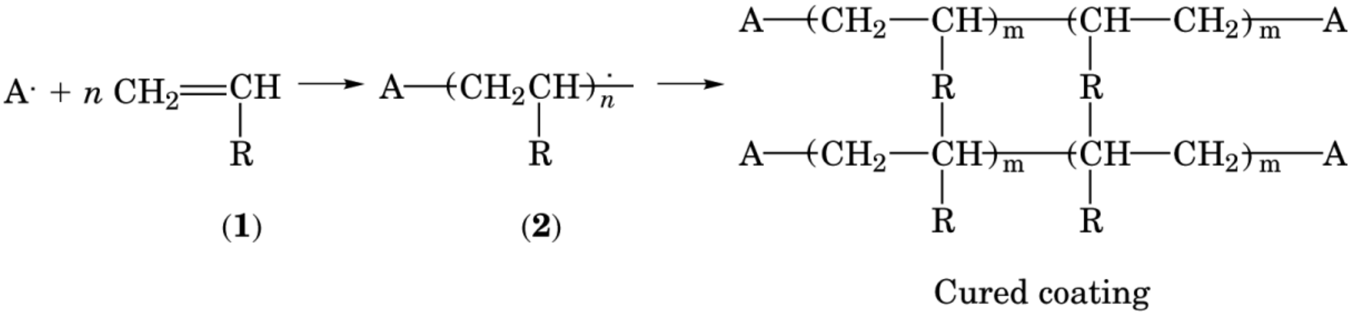


Fig. 2. Conventional thermally cured, organic solvent base coating system.



$$A\cdot + n\,\underset{\substack{|\\ R}}{CH_2{=}CH} \longrightarrow A{-}\!\!\left(\underset{\substack{|\\ R}}{CH_2CH}\right)_{\!n}\!\dot{-} \longrightarrow \begin{array}{c} A{-}(CH_2{-}\underset{\substack{|\\R\\|}}{CH})_m{-}(\underset{\substack{|\\R\\|}}{CH}{-}CH_2)_m{-}A \\ A{-}(CH_2{-}\underset{\substack{|\\R}}{CH})_m{-}(\underset{\substack{|\\R}}{CH}{-}CH_2)_m{-}A \end{array}$$

(**1**) (**2**)

Cured coating

Fig. 3. Polymerization initiation and propagation by radiation-generated free radicals. A is the initiating radical produced by irradiating the liquid coating. (**1**) represents the liquid monomer–unsaturated polymer reactive coating system. R is functional. (**2**) is the growing polymer chain (free radical). The cured coating is a solid polymeric network film structure.

Because electron energies of only 100 eV or less are required to break chemical bonds and to ionize or excite components of the coating system, the shower of scattered electrons produced in the coating leads to a intense population of free radicals throughout the coating. These initiate the polymerization reaction and this polymerization process results in a dry, three-dimensional cross-linked coating (Fig. 3). In this process, most of the energy is absorbed into the coating and is not lost to the substrate, as is the case in thermal curing reactions (5). Neither cobalt-60 nor x-ray energy sources are used in radiation curable coating systems; x-rays are used in photolithographic processes (see Lithographic resist materials (Supplement)).

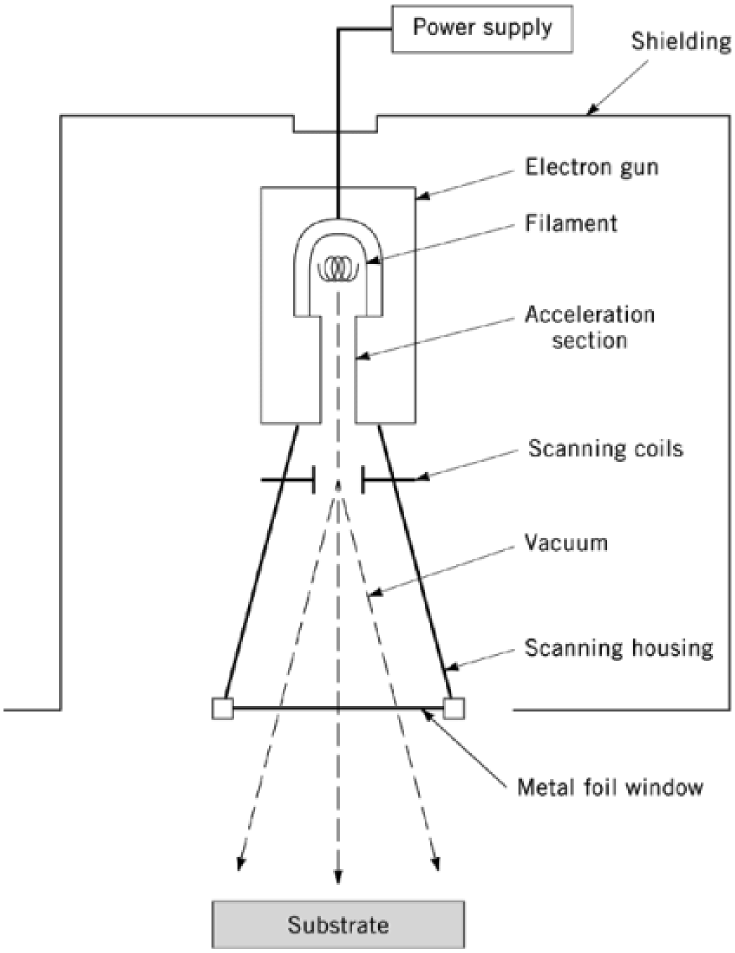


Fig. 4. Scanned electron beam accelerator system.

4.1. Electron Beam

An electron beam processing unit (Fig. 4) consists mainly of a power supply and an electron beam acceleration tube. The power supply increases and rectifies line current and the accelerator tube generates and focuses the beam and controls the electron scanning. The beam is produced when high voltage energizes a tungsten filament, thereby causing electrons to be produced at high rates. These fast electrons are concentrated to form a high energy beam and are accelerated to full velocity inside the electron gun. Electromagnets on the sides of the accelerator tube allow deflection or scanning of the beam as with a television tube. Scanning widths and depths vary from 61–183 cm to 10–15 cm, respectively. The scanner opening is covered with a thin metal foil, usually titanium, that allows passage of electrons but maintains the high vacuum required for high free-path lengths. Characteristic power, current, and dose rates of accelerators are 200–500 kV, 25–200 mA, and 10–100 kGy/s (1–10 Mrad/s), respectively.

Electron processors have several disadvantages. The most severe of these is the large area that must be shielded, because any surface enclosing the electron accelerator scanner acts as a source of x-rays generated by electrons scattered to the wall, and these emissions are along the entire length of the system. Another disadvantage is the large space requirement for housing the equipment.

Advantages of the electron beam processor are its ability to penetrate thick and highly pigmented coatings. It is used to cross-link reactive unsaturated polymers, nonreactive thermoplastic polymers, insulation, and wire-cable coverings (4, 9, 16) (see Insulation, electric–wire and cable coverings).

4.2. Electrocurtain

The electrocurtain processor (Energy Sciences) (Fig. 5) is a high (150 kV) voltage electron tube that provides a continuous strip of energetic electrons from a linear filament or cathode, which is on the axis of symmetry of the system. The cylindrical electron gun shapes and processes the electron stream, in a grid-controlled structure. The stream is then accelerated across a vacuum gap to a metal window where it emerges directly into air and travels onto the product. The energetic electrons from the processor are injected directly in the coating, where they create the initiating free radicals. In the liquid-phase systems, the polymerization process propagates until the activity of the growing chain is terminated. These energetic electrons can penetrate many different types of pigmented coatings and are capable of producing through-cure to the substrate–polymer coating interface. Both the electron beam and the electrocurtain cure pigmented films, but the power of the electrocurtain is substantially less, having a maximum-curing-film thickness range of ca 0.025–0.36 mm.

In the electrocurtain processor, the shielding is clad directly to the tube housing. Housing space is relatively small, because a shielded tube 25 cm in diameter replaces the 3-m high structure required for the scanned electron beam apparatus. The electrocurtain has a more flexible geometry and can be adapted more readily to many different types of curing applications (43).

4.3. Multiple-Planar Cathode Processors

The design criterion for this electron accelerator system is a planar array of concentrated cathode control grid elements. The modular cathode construction allows for broad-beam (250-cm wide) processing of materials using powers of 30 kGy (3 Mrad) at 300 m/min. The system (RPC Industries) also includes integrated shielding and high terminal voltages (44).

4.4. Coatings Ingredients

Ingredients of liquid high energy electron radiation-curable coatings are analogues of components contained in conventional solvent-based thermal-curing coating systems. In conventional solvent-based coatings systems, a preformed polymer (usually 3,000–25,000 mol wt) is dissolved in an organic solvent (30–80% solids), and a cross-linking oligomer and various flow agents, catalysts, pigments, etc, are added. The coating is applied to a substrate by conventional methods, eg, spray, roll coating, and flow coating, and subsequently is cured in gas or ir thermal ovens. Curing of conventional solvent-based coatings involves solvent removal and thermal initiation of chemical reactions between the polymers and cross-linking oligomers that are involved in developing final film properties through three-dimensional network formation of cross-linking sites (45, 46) (see Fig. 2).

4.4.1. Monomers and Cross-Linking Agents or Oligomers

The monomer in high energy electron radiation-curable coatings is the analogue of the solvent in conventional paint. Although, like a solvent, it is a medium for all of the other ingredients and provides the necessary liquid physical properties and rheology, the monomer differs in that it enters the copolymerization and is not lost on cure. Most radiation-curable monomers (ca 100–500 mol wt) contain single unsaturation sites and are high boiling acrylate esters, although in some special coatings styrene can be used as a monomer. Monomers are usually very pure compounds that have well-defined molecular weights and boiling points.

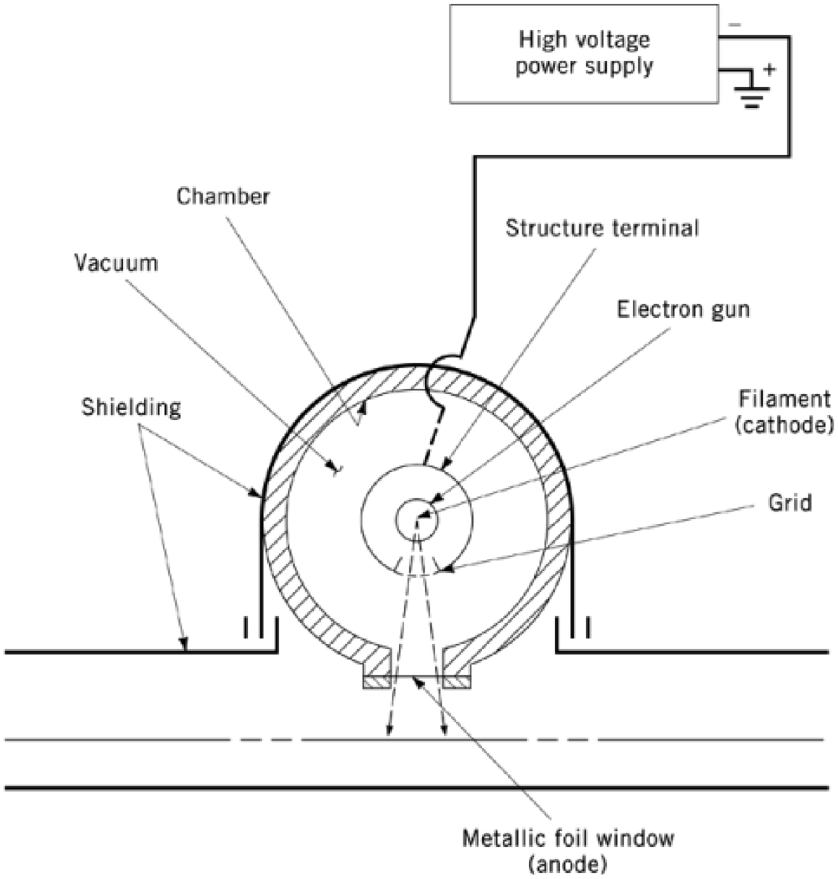


Fig. 5. Planar cathode electrocurtain processor.

Cross-linking agents or cross-linking oligomers in conventional thermosetting coatings formulations are usually melamine resins, ie, they involve acid, hydroxyl transetherification cross-linking; amine–amide hardeners that include oxirane (epoxy) ring opening; and blocked isocyanate prepolymers. The term oligomer represents materials that do not have well-defined molecular weights but rather consist of a distribution of low molecular weight subunits that are associated with the chemical structure of the parent molecule. The term cross-linking agents/oligomers represents molecules that have multiple (two or more) functional groups that can enter into a chemical reaction. Cross-linking agents or oligomers in radiation-curing systems are similar to single, vinyl monomers except they contain di-, tri-, or multifunctional unsaturation sites (ca 200–1000 mol wt). These multifunctional components cause polymer propagation reactions to grow into three-dimensional network structures of a cured film. Monofunctional (single vinyl or acrylic/methacrylic acid ester unsaturation site) monomers include the following (47, 48):

tetrahydrofurfuryl methacrylate or acrylate
cyclohexyl methacrylate or acrylate
n-hexyl methacrylate or acrylate
2-ethoxyethyl acrylate or methacrylate

isodecyl methacrylate or acrylate
2-methoxyethyl acrylate
2(2-ethoxyethoxy)ethyl acrylate
stearyl acrylate or methacrylate
lauryl methacrylate or acrylate
octyl acrylate
2-phenoxyethyl acrylate or methacrylate
glycidyl methacrylate
isobornyl methacrylate or acrylate
benzyl acrylate
isooctyl acrylate
polypropylene glycol monomethacrylate or monoacrylate

Cross-linking agents or oligomers with multifunctional unsaturation sites include the following:

triethylene glycol dimethacrylate or acrylate
ethylene glycol dimethacrylate
tetraethylene glycol dimethacrylate or diacrylate
polyethylene glycol dimethacrylate
1,3-butylene glycol diacrylate or dimethacrylate
1,4-butanediol diacrylate or methacrylate
diethyl glycol diacrylate or dimethacrylate
1,6-hexanediol diacrylate or dimethacrylate
neopentyl glycol diacrylate or dimethacrylate
polyethylene glycol (200) diacrylate
triethylene glycol diacrylate
tripropylene glycol diacrylate
ethoxylated bisphenol A dimethacrylate or diacrylate
di/trimethylolpropane tetraacrylate
ethoxylate trimethylolpropane triacrylate
propoxylated trimethylolpropane triacrylate
propoxylated neopentyl glycol diacrylate
glyceryl propoxy triacrylate
tris(2-hydroxy ethyl) isocyanurate trimethacrylate
pentaerythritol tetraacrylate
trimethylolpropane trimethacrylate or triacrylate
tris(2-hydroxyethyl) isocyanurate triacrylate
dipentaerythritol pentaacrylate

4.4.2. Polymers

The molecular weights of polymers used in high energy electron radiation-curable coating systems are ca 1,000–25,000 and the polymers usually contain acrylic, methacrylic, or fumaric vinyl unsaturation along or

Table 6. Performance Characteristics of Thermally Curable Polymer Backbone Systems

System	Cost	Chemical resistance	Physical properties	Outdoor durability
epoxies	medium	excellent	very good	very poor
acrylics	low–medium	very good	good	very good
polyesters	low	fair–good	very good	good
polyurethanes				
aliphatic	high	very good	excellent	very good
aromatic	high	very good	excellent	very poor

Table 7. Ionizing Radiation Curing of Coatings

Coating composition	Conditions	Reference
65 wt % unsaturated polyester, 35 wt % vinyl monomer[a]	cured using 300-keV electrons at 200 kGy/min[b]	(49, 50)
acrylic copolymers containing pendent unsaturation[c] and 35–45 wt % of a vinyl monomer[a]	cured using a total dosage of 150-kGy[b] electron beam; used to coat plastic substrates	51
acrylate monomers, ie, acrylate unsaturated epoxy and acrylate unsaturated polyurethanes	electron curtain curing; used in general coating applications	52
monomers, ie, polyfunctional vinyl intermediates	metal, wood, and plastic finishing applications using electron-beam processes	(53, 54)
vinyl monomer	^{60}Co-curing of monomer; vacuum impregnation of wood	55

[a] 2-Ethylhexyl acrylate or styrene.

[b] 1 Gy = 100 rad (10 kGy = 1 Mrad)

[c] 0.5–1.75 mol double bonds per 1000 mol wt.

attached to the polymer backbone (4, 48). Aromatic or aliphatic diisocyanates react with glycols or alcohol-terminated polyether or polyester to form either isocyanate or hydroxyl functional polyurethane intermediates. The isocyanate functional polyurethane intermediates react with hydroxyl functional polyurethane and with acrylic or methacrylic acids to form reactive polyurethanes.

The chemical class of the polymer backbone varies with coating requirements, and the different chemical classes give the same overall properties as a related thermal cure coating system (Table 6). Examples of high energy electron or ionizing radiation-curable coating systems, experimental conditions, and their application are listed in Table 7 (46–48). Reactive coating formulation ingredients are *(1)* single-functional vinyl monomers such as 2-ethylhexyl acrylate, styrene, *N*-vinylpyrrolidinone, vinyltoluene, and lauryl methacrylate; *(2)* multifunctional vinyl monomers such as 1,6-hexanediol diacrylate, tetraethylene glycol diacrylate, trimethylolpropane triacrylate, and pentaerythritol triacrylate; and *(3)* unsaturated polymers such as maleic–fumaric acid unsaturated polyesters, acrylic copolymers containing pendent vinyl unsaturation, epoxy acrylates, and polyurethane acrylates.

Reactive (unsaturated) epoxy resins (qv) are reaction products of multiple glycidyl ethers of phenolic base polymer substrates with methacrylic, acrylic, or fumaric acids. Reactive (unsaturated) polyester resins are reaction products of glycols and diacids (aromatic, aliphatic, unsaturated) esterified with acrylic or methacrylic acids (see Polyesters, unsaturated). Reactive polyether resins are typically poly(ethylene glycol (600) dimethacrylate) or poly(ethylene glycol (400) diacrylate) (see Polyethers).

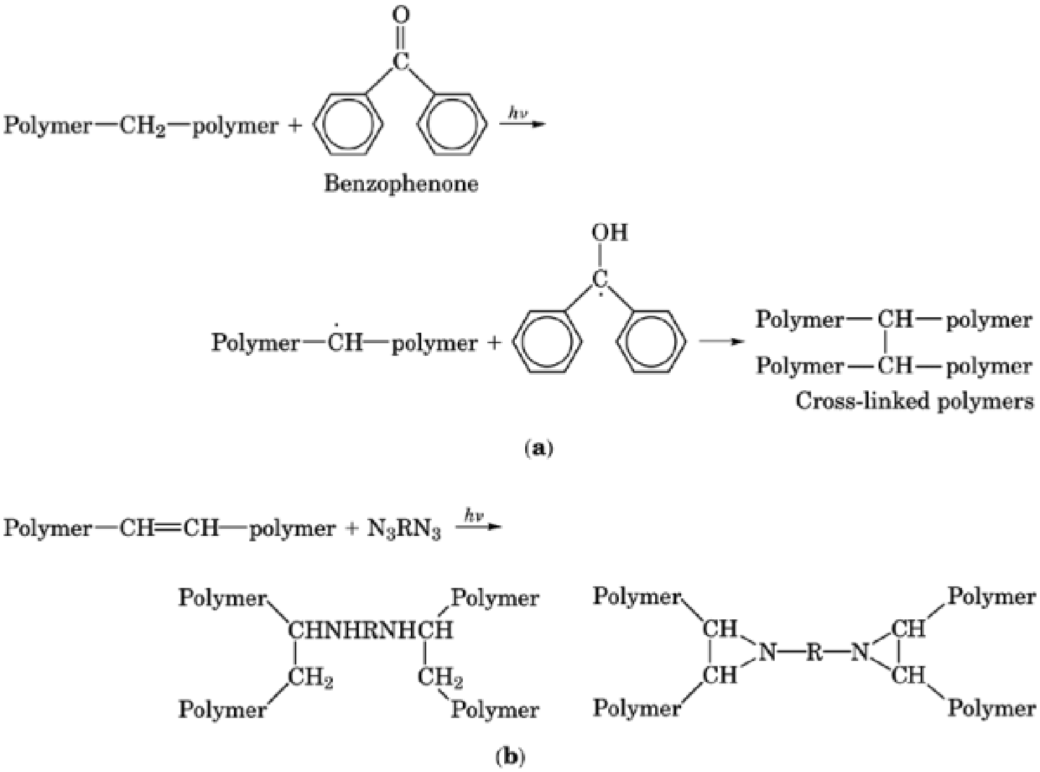


Fig. 6. Coupling of polymer chains via (**a**) photoinduced hydrogen abstraction free-radical reactions and (**b**) nitrene insertion/addition reactions.

5. Curing with Ultraviolet, Visible, and Infrared Processing Equipment

5.1. Polymers

Upon direct absorption of uv or visible wavelengths of light, polymer substrates undergo chain scission and cross-linking. Cross-linking or curing of preformed polymeric materials, ie, thermoplastics, can be markedly enhanced through the use of special photosensitive molecules that are mixed into the polymer matrix or that chemically attach to the backbone of the polymer chains. These special photosensitive molecules absorb uv or visible light energies much more efficiently than the polymer; they rapidly form excited states that undergo photochemical reactions which in turn form reactive free-radical intermediates that effect polymer dimerization or cross-linking. When compounded into the preformed polymer matrix, these special photosensitive molecules, eg, benzophenone, can undergo light-induced radical abstraction or insertion reactions that result in coupling of the polymer chains and in network formation (48, 56, 57) (Fig. 6).

Similar types of cross-linking reactions are observed for polymers to which photosensitive molecules are chemically attached to the backbone of the polymer structure (Fig. 7). Radiation curing of polymers using uv and visible light energies is used widely in photoimaging and photoresist technology (Table 8) (58, 59).

Infrared processing is involved with thermoforming or heat-bonding of thermoplastic polymeric materials together. These polymer heat-forming or melting processes do not usually cure the polymer but only cause physical changes and maintain the original thermoplastic characteristics of the polymer (19).

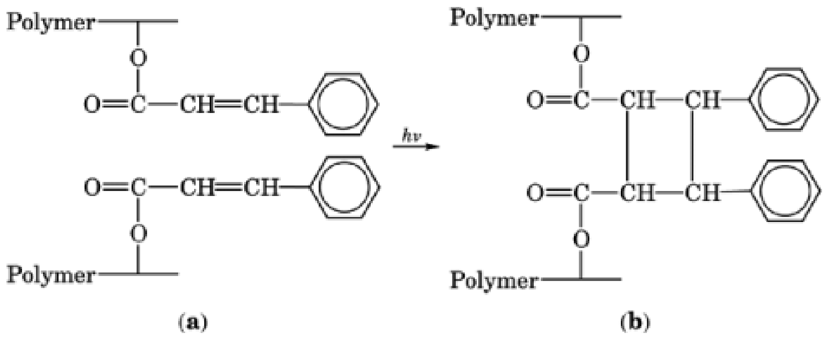
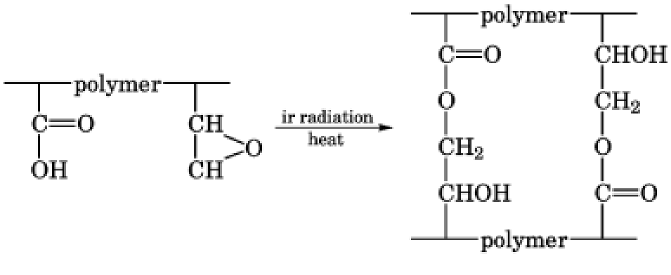


Fig. 7. Photodimerization of light-sensitive functional groups attached to polymer backbone structures: (**a**) polymer containing photosensitive cinnamic ester linkage, and (**b**) cross-linked polymer.

Table 8. Photocurable Polymer Systems For Photoresist Applications

Polymers	Comments	Reference
poly(vinyl cinnamate)s	uv- and visible light-induced photodimerization reactions; used in negative photoresist technologies	60
poly(vinyl cinna-myliden eacetate)s	visible light-induced photodimerization reactions; 50% more efficient than poly(vinyl cinnamate)s	61
polychalcones	photodimerization or addition reactions; used in negative photorest technologies	62
polycoumarins	photodimerization or addition reactions; used in negative photoresist technologies	63
polystilbenes	photodimerization or addition reactions; used in negative photoresist technologies	64
cyclized rubber	cross-linked with bis-azide–nitrene insertion and addition reactions	65
allylic esters	cross-linked with bis-azide–nitrene insertion reactions	66
thiolene polymers	unsaturated polymers (allyl or vinyl functionality) cross-linked with multifunctional mercaptans and photosensitizer molecules	67
phenolic polymers and acid functional acrylic resins	quinone diazide, solubility inhibitors, and photosensitizers for light-induced hydrophobic or hydrophilic reactions associated with positive photoresist technology	(68, 69)

In order to cure, ie, form three-dimensional network structures through chemical changes on polymer systems with ir radiation, it is necessary to design a reactive functionality within the polymer structure so that coupling reactions can take place between the polymer chains as shown in the following reaction:



cross-linked polymer

Table 9. Thermally Curable Polymer Systems

Polymers	Comments	Reference
aromatic epoxy polymers plus acid functional polymers or oligomers	poor outdoor weatherability; good chemical resistance	70
aromatic epoxy polymers plus polyfunctional amines	excellent corrosion resistance	71
hydroxyl-containing polymers and melamine oligomers	good outdoor weatherability	72
hydroxyl-containing polymers plus blocked isocyanates	good outdoor weatherability	71
carboxyl-containing polymers plus oxazolines	good outdoor weatherability	71

Certain polymeric structures can also be blended with other coreactive polymers or multifunctional reactive oligomers that affect curing reactions when exposed to ir radiation. These coreactive polymers and cross-linking oligomers undergo condensation or addition reactions, which cause the formation of network structures (Table 9) (4, 5, 47).

5.2. Coatings

There are five characteristics of uv and visible light energy irradiation or photocuring of coatings: (*1*) the stable light source must be capable of producing uv and visible wavelengths of light, ie, near and far uv (200–400 nm) to visible (400–700 nm), with sufficient power or intensity to be commercially feasible; (*2*) the photoinitiator (PI) must be capable of absorbing uv and visible-light radiation at appropriate wavelengths of energy as emitted from the light source; (*3*) in a free-radical mechanism process, active free-radical intermediates must be produced through the action of light absorption by the photochemically active photoinitiator; these free radicals initiate polymerization of unsaturated monomers, oligomers, and polymers, and photoinitiators are not required in high energy electron-curing processes; (*4*) unsaturated, high boiling acrylate or methacrylate monomers, oligomers, cross-linking agents, and low molecular weight polymers comprise the fluid, low viscosity, light-curable coating system and are similar to the coating materials used in the high energy electron-curing process; and (*5*) after free-radical initiation of the reactive liquid coating system, the monomers propagate into a fully cured, cross-linked solid coatings or films (5, 73, 74).

$$\text{photoinitiator} \xrightarrow{h\nu} [\text{free} - \text{radical intermediates}]$$

$$\begin{array}{c}[\text{free} - \text{radical intermediates}] + \text{unsaturated acrylate monomers,} \longrightarrow \text{cured films}\\ \text{polymers, etc}\end{array}$$

In a cationic photoinitiated reactive system, the photoactive catalyst releases a cation or acid intermediate, which then interacts with low molecular weight epoxy resins or vinyl ether-substituted monomers, oligomers, cross-linkers, and polymers, thus making up the liquid coating composition. After release of the acid or cationic catalyst, the reactive liquid epoxy or vinyl ether coating propagates into a cured film structure in an analogous manner as the free-radical-initiated/cured coating system.

$$\text{photoactive catalysts} \longrightarrow \left[\text{acid or cation intermediates}\right]$$

$$\begin{array}{c}[\text{acid or cation intermediates}] + \text{epoxy resins or unsaturated vinly} \longrightarrow \text{cured films}\\ \text{ether monomers, polymers, etc}\end{array}$$

These photoinitiators or photocatalysts are usually added to the reactive coating formulations in concentration ranges from less than 1 to 20 wt % based on the total formulation.

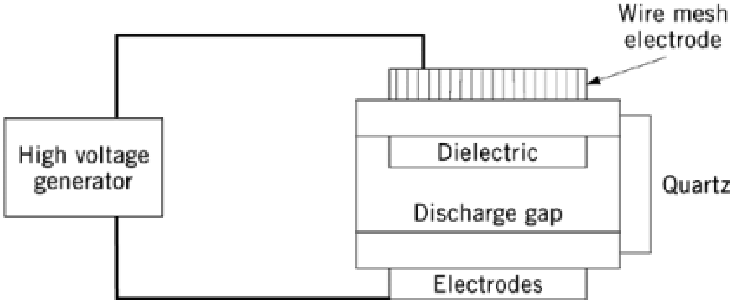


Fig. 8. Schematic of a silent discharge lamp.

5.3. Light Source

The light source normally used in commercial photocuring reactions is the medium pressure mercury arc lamp having a quartz or Vicor envelope. These lamps may contain electrodes for electrical-to-light energy conversion or may be electrodeless, in which case a radio-frequency wave causes mercury atom excitation and subsequent light emission. The normal power input levels are 40–160 W/cm arc length, resulting in sharp peak outputs having ca 10-nm bandwidths. The main peaks are at 313, 365, 404, 436, 546, and 578 nm, with relative outputs of between 2–80 W/cm over the length of the arc. Many other types of uv and visible light sources can be used for photopolymerization reactions, eg, low pressure mercury arcs, flash lamps, fluorescent or germicidal lamps, and lasers (qv).

A different type of light source based on silent electrical gas discharge phenomena has been developed by Asea Brown Boveri Corporation (75). Ultraviolet light radiation is generated in these types of lamps through the formation of excited molecular complexes (excimers or exciplexes) that do not have stable ground states. These excimers can be created in electrical discharges in a rare-gas (helium, neon, argon, krypton, xenon) environment. Because these exciplexes are unstable, they disintegrate within a nanosecond time frame and undergo a spontaneous emission of light energy. A silent discharge configuration allows the maintenance of a high pressure nonequilibrium discharge in which the plasma can be optimized to sustain a stable excimer formation process. A silent discharge configuration has at least one insulator or dielectric barrier, a transparent gas containment compartment, and a space between the electrodes (Fig. 8).

Discharges initiate in the gap region between the electrodes and then spread into surface discharges at the surface of the dielectric layer. The bright surface discharges are on the order of a few mm in diameter and the power ranges from these lamps can be from a few watts to several kilowatts over a variety of narrow wavelengths of light energy. Complete reviews of light sources used in photopolymerization reactions are available (17, 18, 76).

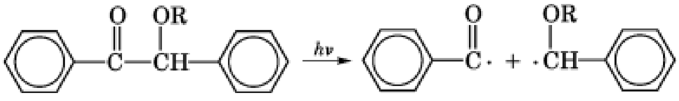
Light-wavelength output energies from various sources are small compared to electron-beam or electrocurtain processors (2–5 to thousands of eV). The energy associated with 365-nm wavelengths of light is equivalent to 3.4 eV or 343 kJ/mol (82 kcal/mol) and is sufficient to cause selective carbon bond rearrangements and cleavage of aromatic carbonyl–alkyl carbon bonds (aromatic C(O)–alkyl) (77).

Light energy alone is not sufficient to cause direct, efficient monomer initiation reactions. Commercial light-induced curing reactions require the use of a special photosensitive compound in the coatings formulation. These photosensitive compounds or photoinitiators are an integral part of the formulation and the cost of a light-sensitive radiation-curable coating system. The type and amount of photoinitiator also influences the relative rate of cure and the final properties of the cured film or coating.

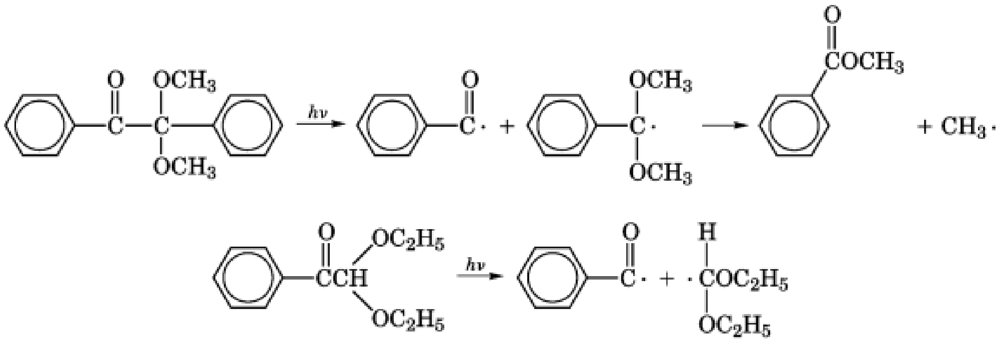
5.4. Photoinitiators

Many theories of photoinitiated polymerization reactions using different light-sensitive catalysts have been reviewed (77–80). There are two general classes of photoinitiators: those that undergo direct photofragmentation upon exposure to uv or visible light irradiation and produce active free-radical intermediates, and those that undergo electron transfer followed by proton transfer to form a free-radical species. The absorption bands of the photoinitiators should overlap the emission spectra of the various commercial light sources (80).

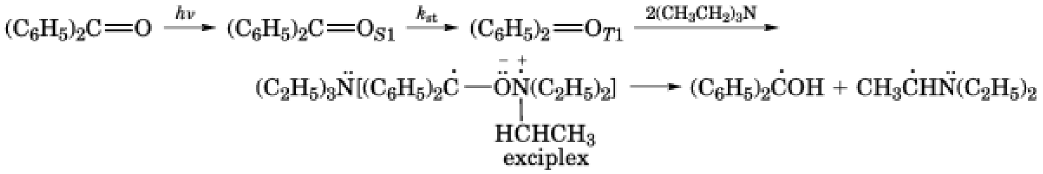
The alkyl ethers of benzoin undergo direct photofragmentation upon absorption of uv energy at ca 360 nm to produce two free-radical intermediates.



Other similar structures undergo the following photofragmentation rearrangement decomposition processes:



The second type of photoinitiators, ie, those that undergo electron transfer followed by proton transfer to give free-radical species, proceed as follows, where k_{st} is the rate constant for intersystem crossing.



$$(C_6H_5)_2C{=}O \xrightarrow{h\nu} (C_6H_5)_2C{=}O_{S1} \xrightarrow{k_{st}} (C_6H_5)_2{=}O_{T1} \xrightarrow{2(CH_3CH_2)_3N}$$

$$(C_2H_5)_3\ddot{N}[(C_6H_5)_2\dot{C}{-}\underset{\text{exciplex}}{\underset{\text{HCHCH}_3}{\overset{-\ +}{\ddot{O}N}}}(C_2H_5)_2] \longrightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}H\ddot{N}(C_2H_5)_2$$

Benzophenone in its ground state (S_0) undergoes absorption of uv energy (340–360 nm) and is excited to its singlet excited states (S_1) followed by intersystem crossing ($k_{st} \cong 1$) to its triplet excited state (T_1). From the triplet excited state, benzophenone forms an encounter complex, or exciplex, with the ground-state alkyl amine, which then undergoes electron transfer from the nitrogen to the excited carbonyl followed by proton transfer from the carbon α to the nitrogen atom. This results in reduction of the benzophenone to form the semibenzpinacol radical and radical formation on the carbon α to the nitrogen atom. Both of these free-radical species can initiate or terminate polymerization of acrylic monomers. These free-radical species can also cross-couple or dimerize to form unreactive compounds. Excited-state aromatic ketones can abstract hydrogen atoms directly from the backbone structure of ethers and other organic substrates. These hydrogen radical abstraction reactions can lead to initiation or termination of the polymerization process. Photoinitiators having absorption capabilities in the visible light energy range are based on dyes, quinones, diketones, and heterocyclic chemical structures (80).

Examples of typical photoinitiator systems used to cure reactive coating systems are as follows (80, 81). The reactive systems are primarily unsaturated acrylic acid esters of different alcohol and polymer structures.

Photoinitiators (electron transfer)	Photoinitiators (photofragmentation)
benzophenone	alkyl ethers of benzoin
halogenated benzophenones	benzil dimethyl ketal
amino functional benzophenones	α-hydroxyacetophenone
fluorenone derivatives	2-hydroxy-2-methylphenol-1-propanone
anthraquinone derivatives	2,2-diethoxyacetophenone
xanthone derivatives	1-phenyl-1,2-propanedione-2-(O-ethoxy-carbonyl) oxime
thioxanthone derivatives	
camphorquinone	2-methyl-1-(4-methylthio) phenyl)-2-morpholino propanone-1
benzil	
diphenoxy benzophenone	2-benzyl-2-*N*,*N*-dimethylamino-1-(4-morpholinophenyl) butanone
	α-amino acetophenones
	halogenated acetophenone derivatives
	sulfonyl chlorides of aromatic compounds
	acylphosphine oxides and bis-acyl phosphine oxides
	bisimidazoles

6. Photoactive Catalysts for Acid or Cation Generators

A variety of monomer and polymer structures can polymerize (cure) when exposed to an acid or cation intermediate species.

$$\left.\begin{array}{l}\text{tetrahydrofuran}\\ \text{epoxy resins}\\ \text{vinyl ethers}\\ \text{styrene}\end{array}\right] \xrightarrow[\text{intermediates}]{\text{acid/cation}} \text{polymer formation}$$

The photoactive catalyst systems commonly used to cure epoxy resins and multifunctional vinyl ether materials include aryldiazonium salts ($\text{ArN}{=}\text{N}^{+}\text{X}^{-}$), and triarylsulfonium and diaryliodonium salts ($\text{Ar}_3\text{S}^{+}\text{X}^{-}$ and $\text{Ar}_2\text{I}^{+}\text{X}^{-}$). Other cation-intermediate-generating catalyst systems are cyclopentadienyl iron(II)–arene hexafluorophosphate complexes, phenylphosphonium benzophenone salts, and pentafluoro phenyl borate anions associated with aryl sulfonium cations (81). An example of how these photoactive catalyst materials initiate the cure of an epoxy functional monomer or polymer is shown in Figure 9. These types of acid-initiated curing reactions for epoxy resins and vinyl ether containing monomers or polymers have been used in coatings and photoresist and printed circuit technologies (78, 81) (see Epoxy resins).

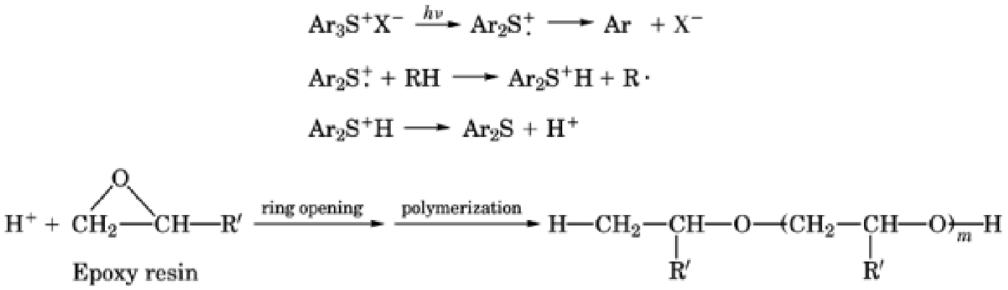


Fig. 9. Initiation of epoxy cure. Irradiation of a triaryl sulfonium salt produces a radical cation that reacts with an organic substrate RH to produce a cation capable of releasing a proton. The proton initiates ring-opening polymerization. $X^-=BF_4^-$, PF_6^-, AsF_6^-, and $S_6F_6^-$.

7. Formulation Design for Free-Radical Cured Systems

Light-induced (free-radical intermediates), radiation-curable coating systems are similar to those used in high energy, electron-radiation-cured coating materials. The reactive coating ingredients in both the light and high energy electron curing processes utilize combinations of single vinyl unsaturated monomers, multifunctional vinyl-substituted cross-linking oligomers, and a variety of unsaturated polymer structures. The only significant difference between high energy cured coatings and light energy cured coatings is the use of a photoinitiator that absorbs the light energy and initiates the start of the curing process.

Although the primary function of the single vinyl ((meth)acrylate) unsaturated monomer component in the formulation is to lower the viscosity of the coating system, the choice of monomer, however, can strongly influence the adhesion of the cured coating to the substrate, the surface energy of the formulation, the barrier properties of the cured film, and the kinetic cure-rate response capability for the entire system. Cross-linking agents or oligomers (multifunctional vinyl or acrylate unsaturated structures) in the formulation tend to give rapid cure rates (formation of three-dimensional networks) and hard surfaces, but strongly contribute to the shrinkage of the final film structure during and after the curing process takes place. This shrinkage of the film produces internal stresses that lead to a loss of adhesion of the coating to the surface of the substrate (82).

High molecular weight polymeric materials in the coating formulation increase the viscosity of the reactive liquid coating system, which strongly influences the method of applying the coating to a substrate. High molecular weight polymers in a coating formulation impart toughness, flexibility, and adhesion capabilities to a cured film structure.

An idealized formulation guideline showing possible interaction of single vinyl unsaturated monomers, multifunctional unsaturated vinyl cross-linking agents or oligomeric molecules, and higher molecular weight polymeric materials is represented by Figure 10.

The design of a commercial coating formulation relies heavily on the science and technology associated with the design of monomers, cross-linking oligomers, and polymers that have an optimized balance of chemical and physical properties for a specific product or application. Empirical correlations of chemical structures of monomers, oligomers, and polymers with their chemical and physical properties have been developed; advanced experimental design techniques are increasingly used to create complex coating compositions that can contain as many as 30 variables in the final system (82–85).

The majority of the commercial radiation-curable coating systems (high energy electron and light-cured coating systems) are clear or contain silica for lowering the surface gloss properties of the final cured film structure. The addition of colorizing pigments or opacifying and extended pigments (titanium dioxide, metal carbonates, etc) to a high energy electron coating formulation usually has only a minor effect on the overall cure rate and the final film performance capabilities of the total system. This is not the case, however, for pigmented

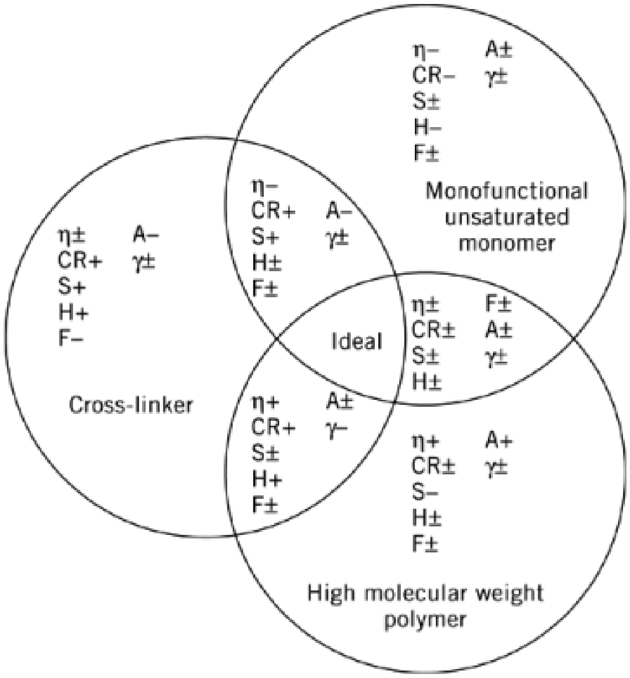


Fig. 10. Generalized formulation design outline for radiation-curable coatings and adhesive systems. The cross-linker is a multifunctional unsaturated cross-linking agent or oligomer. η=viscosity; CR=cure rate; S=shrinkage; H=hardness; F=flexibility; A=adhesion; γ=surface energy; +=increase; and −=decrease.

coatings and inks that are cured with ultraviolet light energy. Many pigments commonly used in decorative coating formulations have large light absorption as well as scattering and reflectance properties that interfere with the ability of the photoinitiator to absorb the light energy required to initiate the polymerization reactions which ultimately create the final cured film structure. Thus, in pigmented coating formulations that are cured by ultraviolet light energies, the special photoinitiator systems being selected must have either the ability to absorb energy directly in the presence of a pigment that has the same absorption bands (the photoinitiator must then have a higher extinction coefficient than the pigment at the same maximum absorbance wavelength), or an absorption band that is outside the region where the pigment absorbs the light energy (86).

Examples of typical coating compositions and their applications in high energy, electron-radiation-curable systems (no photoinitiator required) and light-induced (photoinitiator required) curing reactions are available (87). Although the coating formulation for a photoinitiated acid/cationic curing resin system uses the same methodology and experimental design constraints as those described for the radiation curing of coatings based on free-radical intermediate reactions, the polymers and materials used in the cationic/acid curing system consist of single functional vinyl ethers or epoxy monomers, multifunctional vinyl ethers, and epoxy resins and polymers.

8. Applications and Markets

Since the early 1980s, the conversion of electrical energy into infrared, ultraviolet, and high energy electromagnetic radiation has gained worldwide acceptance as an efficient and economical method for modifying polymeric materials. These radiation-modified polymer systems are associated with many different types of products produced under a wide diversity of manufacturing operations. From a consumer point of view, almost every day a polymeric product that has been manufactured or processed by some form of radiation energy is encountered, for example:

Wood furniture (ir-, electron beam-, and uv-curable coatings)
Beer and beverage can labels (ir- and uv-curable inks)
Metal pipe coatings (uv-curable coatings)
Packaging, eg, paper, foil, and film (uv and electron-beam inks and coatings)
Floor coatings (uv-curable coatings)
Printed publications (ir- and uv-curable inks)
Graphic screen printing ink applications on mirrors (uv-curable inks)
Foamed plastic insulation (electron-beam-irradiated plastics)
Adhesive tapes (electron-beam-cured adhesives)
Rubber tires (electron-beam-irradiated rubber)
Food packaging (electron-beam-irradiated polyolefins)
Wire (electron-beam-irradiated polyolefins)
Telephone cable and optical fibers (uv-curable coatings)
Computers (uv and electron-beam polymer resist materials)
Recording tape (electron-beam-curable coatings)

A summary of applications, markets, and products where radiation-curing technologies have found commercial success may be summarized as follows:

Adhesives (82)
  anaerobics
  pressure sensitive adhesives (PSA)
  hot melt PSA
  flocks
  adhesives and encapsulants
  optical fiber coatings and adhesives
  wire and cable coatings
  dry film solder masks
  magnetic and optical media
Coatings (48)
  furniture coatings
  “no wax” floor tile coatings
  protective topcoats
  metal decoration
  particle board sealer
  coil coatings
  beverage can coatings

    - urethane automotive coatings
    - glass coatings
    - coatings on plastics
- Electronics (9)
    - integrated circuits
    - photoresists and photolithography
    - marking masks
    - conformal coatings
- Inks (88)
    - letterpress
    - screen
    - flexographic
    - lithographic
    - gravure
- Packaging (paper and plastic)
    - packaging adhesives
    - release coatings
    - barrier coatings
- Photochemical machining (89)
    - micromechanical parts
    - optical waveguides
    - three-dimensional model production (stereolithography)

8.1. Infrared Radiation Curing of Coatings

Thermal curing of a conventional coating system requires solvent removal and chemical cross-linking of polymers or oligomers. Commercial processors emit short wavelengths (0.7–2.0 μm), medium wavelengths (2–4 μm), and long wavelengths (4–1000 μm) of infrared radiation. The shortwave ir is near the visible end of the spectrum and, therefore, higher in energy and more penetrating than either the medium or the long wavelength emissions. The shortwave ir radiation is also reflective and can be focused for improved efficiency. A possible difficulty in using shortwave ir processing equipment is the substrate color selectivity characteristics. A dark-colored substrate or coating absorbs more thermal energy than a light-colored substrate; such color selectivity can lead to differential curing processes. Medium wavelengths of ir radiation are not substrate-color-sensitive, but are more difficult to control in terms of reflection or focusing, and somewhat less efficient for certain coating cure requirements than shortwave ir radiation (90). Many conventional coatings systems, such as powder coatings and single- and two-component 100% reactive liquid epoxy or polyurethane coatings, that contain polymer functionalities which cure through thermal processes involved with gas-fired oven technologies (see Tables 6 and 9) can also be cured or processed efficiently using ir radiation energies (91).

9. Curing with Microwave or Radio-Frequency Processing Equipment

Polymer surfaces can be easily modified with microwave or radio-frequency-energized glow discharge techniques. The polymer surface cross-links or oxidizes, depending on the nature of the plasma atmosphere.

Oxidizing (oxygen) and nonoxidizing (helium) plasmas can have a wide variety of effects on polymer surface wettability characteristics (92).

One particularly promising approach to the development of improved coatings for use as metal primers, in fiber treatment, in packaging materials, etc, involves the use of vacuum plasma deposition techniques. Thin (micrometers thick), pinhole-free, polymeric coatings can be developed from a variety of organic moieties, both monomeric and nonmonomeric. Depending on the applications, such coatings can be developed to provide corrosion protection, abrasion and chemical resistance, improved adhesion, barrier properties, etc. With the plasma technique, both capacitively coupled and inductively coupled radio-frequency-energized vacuum chambers can be used for the deposition. In the capacitively coupled chamber, the substrate to be coated is attached to one of the electrodes. Monomer is then introduced into the chamber such that an operating pressure of ca 13 Pa (ca 0.1 mm Hg) is maintained. A glow discharge between the electrodes polymerizes a coating on the substrate. In the inductively coupled reactor, radio-frequency energy is supplied by coils surrounding the chamber. The glow discharge, therefore, fills the entire chamber and coats any item placed in the chamber.

Plasma deposition has been used to prepare acrylic, silicone, and fluorocarbon coatings on a variety of substrates in thicknesses of up to ca 8 μm. Coating variables include applied power, substrate temperature, deposition time, and monomer pressure. The coatings are similar to those produced from the same monomers by conventional polymerization techniques. However, there are structural differences and the resulting coatings are highly cross-linked. All exhibit excellent chemical resistance and good adhesion to the different substrates. Certain coatings have good optical clarity. Coating hardness appears to vary appreciably with monomer type and deposition conditions (9, 22, 23, 93, 94).

Plasma processing technologies are used for surface treatments and coatings for plastics, elastomers, glasses, metals, ceramics, etc. Such treatments provide better wear characteristics, thermal stability, color, controlled electrical properties, lubricity, abrasion resistance, barrier properties, adhesion promotion, wettability, blood compatibility, and controlled light transmissivity.

BIBLIOGRAPHY

"Radiochemical Technology" in *ECT* 2nd ed., Vol. 17, pp. 53–64, by W. H. Beamer, The Dow Chemical Co.; "Radiation Curing" in *ECT* 3rd ed., Vol. 19, pp. 607–624, by V. D. McGinniss, Battelle Columbus Laboratory.

Cited Publications

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, John Wiley & Sons, Inc., New York, 1962.
2. J. E. Wilson, *Radiation Chemistry of Monomers, Polymers, and Plastics*, Marcel Dekker, Inc., New York, 1974.
3. A. Singh and J. Silverman, eds., *Radiation Processing of Polymers*, Hanser Publishers, New York, 1992; L. F. Rossetti, AFP-SME Technical Paper, "Irradiated Wave, Cable and Tubing," Association for Finishing Processes of SME, FC76-510, Society of Manufacturing Engineers, Dearborn, Mich., 1976.
4. V. D. McGinniss, L. J. Nowacki, and S. V. Nablo, *ACS Symposium* **107**, 51–70 (1979).
5. V. D. McGinniss, *National Symposium on Polymers in the Service of Man*, American Chemical Society, Washington, D.C., 1980, 175–180.
6. G. A. Senich and R. E. Florin, *J. Macromol. Sci.* **C24**(2), 240–324 (1984).
7. J. C. Colbert, ed., *Modern Coating Technology: Radiation Curing, Electrostatic, Plasma, and Laser Methods, Chemical Technology*, Noyes Data Corp., Park Ridge, N.J., 1982.
8. D. R. Randell, ed., *Radiation Curing of Polymers*, Royal Society of Chemistry, Burlington House, London, 1987.
9. V. D. McGinniss, "Radiation Curing: State-of-the-Art Assessment," Report prepared for the Electric Power Research Institute, Palo Alto, Calif., EPRI Report No. EM-4570, 1986.
10. James H. O'Donnell, ed., *Irradiation of Polymeric Materials: Processes, Mechanisms and Applications*, American Chemical Society, Washington, D.C., 1993.

11. J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry*, John Wiley & Sons, Inc., New York, 1964.
12. A. Danno, in A. Danno, *Radiation Chemistry and Its Applications*, IAEA Technical Report Series No. 84, International Atomic Energy Agency, Vienna, Austria, Apr. 1967, p. 2341.
13. S. Jefferson and co-workers, in S. Jefferson and co-workers, *Advances in Nuclear Science and Technology*, Vol. **4**, Academic Press, New York, 1968, 335–338.
14. G. W. Grodstein, *X-Ray Attenuation Coefficients from 10 keV to 100 MeV*, Circ. 583, U.S. National Bureau of Standards, Washington, D.C., 1957.
15. Richard Bradley, *Radiation Technology Handbook*, Marcel Dekker, Inc., New York, 1984.
16. A. F. Readdy, Jr., "Application of Ionizing Radiations in A. F. Readdy, Jr., "Application of Ionizing Radiations A. F. Readdy, Jr., "Application of Ionizing Radiations in Plastics and Polymer Technology," Plastic Report R41, Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, N.J., 1971.
17. W. E. Elanbass, *Light Sources*, Crane, Russak & Co., Inc., New York, 1972.
18. V. D. McGinniss, in S. P. Pappas, ed., *UV Curing Science and Technology*, Technology Marketing Corp., Stamford, Conn., 1978, 96–132.
19. A. F. Readdy, Jr., *Plastics Fabrication by Ultraviolet, Infrared, Induction, Dielectric and Microwave Radiation Methods*, Plastic Report R43, Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, N.J., 1972.
20. R. W. Pray, *A New Look at Infrared*, SME Publication FC78-543, Association for Finishing Processes of SME, Dearborn, Mich., 1978.
21. J. R. Bush, "Electric Infrared Process Heating: State-of-the-Art Assessment," Report prepared for the Electric Power Research Institute, Palo Alto, Calif., EPRI Report No. EM-4571, 1986.
22. J. R. Hollahan and A. T. Bell, *Techniques and Applications of Plasma Chemistry*, John Wiley & Sons, Inc., New York, 1974.
23. M. Shen and A. T. Bell, eds., *Plasma Polymerization*, American Chemical Society, Washington, D.C., 1979.
24. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co., Menlo Park, Calif., 1978.
25. Charles E. Hoyle and James F. Kinstle, eds., *Radiation Curing of Polymeric Materials*, American Chemical Society, Washington, D.C., 1990.
26. R. O. Bolt and J. D. Carroll, *Radiation Effects on Organic Materials*, Academic Press, Inc., New York, 1963.
27. J. F. Kinstle, *Paint Varn. Prod.* **63**(6), 17 (1973).
28. S. P. Pappas, ed., *Radiation Curing Science and Technology*, Plenum Press, New York, 1992.
29. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.* **16**, 2291 (1972).
30. G. Alder, *Science*, **141**, 321 (1963).
31. G. Odian and B. S. Bernstein, *Nucleonics*, **21**, 80 (1963).
32. G. F. D'Alelio, R. Haberli, and G. F. Pezdirtz, *Effect of Ionizing Radiation on a Series of Saturated Polyesters*, NASA-SP-58, National Aeronautics and Space Administration, Washington, D.C., 1964.
33. V. D. McGinniss, in H. F. Mark and co-workers, eds., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **4**, 418–449, John Wiley & Sons, Inc., New York, 1986.
34. B. S. Bernstein and co-workers, *J. Appl. Polym. Sci.* **10**, 143 (1966).
35. B. S. Bernstein and J. Lee, *Ind. Eng. Chem. Prod. Res. Deu.* **6**, 211 (1967).
36. M. Izumi and co-workers, *Sumitomo Electr. Tech. Res.* **9**, 50 (Mar. 1967).
37. V. L. Lanza and R. M. Halperin, *Proceedings of 13th Annual Symposium on Communication Wires and Cables*, Asbury Park, N.J., Dec. 1963.
38. "Self-Adhering Silicone Rubber Tape" in *General Electric Company Bulletin*, Insulating Materials Data PD 1302, General Electric Co., Schenectady, N.Y.
39. V. L. Lanza and P. M. Cook, *Proceedings of 9th Annual Symposium on Communication Wire and Cable*, Asbury Park, N.J., Nov.–Dec. 1960.
40. R. C. Becker, *Plast. World*, **35**, 48 (Feb. 1977).
41. "Photopolymers: Principles, Processes and Materials," *Proceedings of Regional Technical Conference of the Society of Plastic Engineers*, Ellenville, N.Y., 1976.
42. A. Banov, *Paints and Coatings Handbook*, Structures Publishing Co., Farmington, Mich., 1978.
43. S. V. Nablo, SME Technical Paper, FC75-311, Society of Manufacturing Engineers, Dearborn, Mich., 1975.
44. W. J. Ramler, *J. Radiat. Curing*, **1**(3), 129–135 (Aug. 1984).
45. A. J. Chompff and S. Newman, eds., *Polymer Networks*, Plenum Press, New York, 1971.

46. A. R. Shultz, in E. M. Fettes, eds., *Chemical Reactions of Polymers*, John Wiley & Sons, Inc., New York, 1964; R. W. Tess and G. W. Pochlein, ed., *Applied Polymer Science*, 2nd ed., American Chemical Society, Washington, D.C., 1985.
47. J. L. Gardon and J. W. Prane, eds., *Nonpolluting Coatings and Coating Processes*, Plenum Press, New York, 1973.
48. P. K. T. Oldering, ed., *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints*, SITA Technology, Ltd., London, 1991, Vols. **I–IV**; Sartomer Monomer/Oligomer Photoinitiator Product Line Literature, Sartomer Co., Exton, Pa., 1991; D. H. Solomon, *The Chemistry of Film Formers*, John Wiley & Sons, Inc., New York, 1967.
49. W. Burlant and J. H. Hinsch, *J. Polym. Sci.* **A2**, 2135 (1964).
50. *Ibid.*, **A3**, 3587 (1965).
51. S. S. Labana and E. O. McLaughlin, *J. Elastoplast.* **2**, 3 (1970).
52. S. V. Nablo and E. P. Tripp, *Radiat. Phys. Chem.* **9**, 325 (1977).
53. T. J. Miranda and T. F. Huemmer, *J. Paint Technol.* **41**, 118 (1969).
54. K. H. Morganstern, *Proceedings of SAE Engineering Congress*, Detroit, Mich., 1967.
55. J. H. Frankfort, *Proceedings of Information Meeting on Irradiated Wood-Plastic Materials*, Report ORNL-11C-7, Chicago, Ill., 1965.
56. S. S. Labana, ed., *Ultraviolet Light Induced Reactions in Polymers*, American Chemical Society, Washington, D.C., 1976.
57. *Radiation Curing in Polymer Science and Technology*, Vols. **I–IV**, J. P. Fouassier and J. F. Rabek, eds., Elsevier Science Publishing Co., Inc., New York, 1993.
58. E. D. Feit, in S. P. Pappas, ed., *UV Curing: Science and Technology*, Technology Marketing Corp., Stamford, Conn., 1978, 229–256.
59. L. F. Thompson and M. J. Bowden, *Introduction to Microlithograph*, 2nd ed., American Chemical Society, Washington, D.C., 1994; H. Ito, S. Tagawa, and K. Horie, eds., *Polymeric Materials for Microelectronic Applications: Science and Technology*, American Chemical Society, Washington, D.C., 1995.
60. K. Nakamura, T. Sakata, and S. Kikuchi, *Bull. Chem. Soc. Jpn.* **41**, 1765 (1968).
61. T. A. Shankoff and A. M. Trozzolo, *Photo. Sci. Eng.* **19**, 143 (1975).
62. M. Tsuda, *J. Polym. Sci.* **A2**, 2907 (1964).
63. G. A. Delzenne, in N. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Supp. 1, John Wiley & Sons, Inc., New York, 1976.
64. F. A. Stuber and co-workers, *J. Appl. Polym. Sci.* **13**, 2217 (1969).
65. F. C. Deschryver, N. Boens, and G. Smith, *J. Polym. Sci.* **A1**, 1939, 1970.
66. S. Shimizm and G. R. Bird, *J. Electrochem. Soc.* **124**, 1394 (1977).
67. W. S. DeForest, *Photoresists: Materials and Processes*, McGraw-Hill Book Co., Inc., New York, 1975.
68. J. Kosar, *Light-Sensitive Systems*, John Wiley & Sons, Inc., New York, 1965, 194–320.
69. L. F. Thompson, C. G. Wilson, and J. M. J. Frechet, *Materials for Microlithography*, American Chemical Society, Washington, D.C., 1984; M. Biswas and T. Uryu, *J. Macromol. Sci.* **C26**(2), 249–352 (1986).
70. U.S. Pat. 3,888,943 (June 10, 1975), S. S. Labana (to Ford Motor Corp.).
71. S. Gabriel, *J. Oil Col. Chem. Assoc.* **59**, 52 (1976).
72. N. J. H. Gulpen and A. J. VanDeWerff, *J. Paint Technol.* **47**, 81 (1975).
73. V. D. McGinniss and D. M. Dusek, *J. Paint Technol.* **46**, 23 (1974).
74. C. G. Roffey, *Photopolymerization of Surface Coatings*, John Wiley & Sons, Inc., New York, 1982; C. Decker and K. Moussa, *J. Coatings Tech.* **65**(819), 49–57 (1993).
75. U. Kogelschatz, *Appl. Surface Sci.* **54**, 410–423 (1992).
76. L. R. Koller, *Ultraviolet Radiation*, John Wiley & Sons, Inc., New York, 1965.
77. J. Kopecky, *Organic Photochemistry: A Visual Approach*, VCH Publishers, Inc., New York, 1992; S. P. Pappas and V. D. McGinniss, in Ref. 45, Chapt. 1, 1–22.
78. V. D. McGinniss, *Photogr. Sci. Eng.* **23**(3), 124 (1979).
79. V. D. McGinniss, *J. Radiat. Curing*, **2**, 3 (1975).
80. V. D. McGinniss, *Develop. Polym. Photochem.* **3**, 1–52 (1982); H. J. Hageman, *Prog. Org. Coatings*, **13**, 123, 1985.
81. C. Chang and co-workers, in L. J. Calbo, ed., *Handbook of Coatings Additives*, Vol. **2**, Marcel Dekker, Inc., New York, 1992; J. V. Crivello and J. H. W. Lam, *J. Polym. Sci.* **17**, 977 (1979); J. L. Dektar and N. P. Hacker, *J. Chem. Soc. Chem. Commun.*, 1591 (1987); C. Priou and co-workers, *Polym. Mat. Sci. Eng.* **72**, 417, 1995.

82. V. D. McGinniss and A. Kah, *Polym. Eng. Sci.* **17**(7), 478–483 (1977); V. D. McGinniss, in L. H. Lee, ed., *Adhesive Chemistry*, Plenum Publishing Corp., 1984, 363–377.
83. V. D. McGinniss, *Org. Coatings Plast. Chem.* **39**, 529–537 (1978); V. D. McGinniss, *Org. Coatings Appl. Polym. Sci.* **46**, 214–223 (1982).
84. D. W. VanKrevelen, *Properties of Polymers*, Elsevier Science Publishing Co., Inc., New York, 1972.
85. G. C. Derringer, *J. Quality Tech.* **12**(4), 214–219 (1980).
86. V. D. McGinniss, in S. S. Labana, ed., *International Symposium of UV Light-Induced Polymer Reactions*, American Chemical Society, Washington, D.C., 1976.
87. C. H. Carder, *Paint Varn. Prod.* **64**(8), 19 (1974).
88. S. G. Wentink and S. D. Koch, eds., *UV Curing in Screen Printing for Printed Circuits and the Graphics Arts*, Technology Marketing Corp., Norwalk, Conn., 1981.
89. P. F. Jacobs, *Rapid Prototyping and Manufacturing: Fundamental of Stereolithography*, Society of Manufacturing Engineers, Dearborn, Mich., 1992.
90. W. C. Hankins, *J. Oil. Col. Chem. Assoc.* **60**, 300 (1977).
91. R. J. Dick and co-workers, *J. Coatings Tech.* **66**(831), 23–38 (1994).
92. J. F. Kinstle, *J. Radiat. Curing*, **2**(2), 15 (1975).
93. V. D. McGinniss, *Proceedings of 20th International Conference in Organic Coatings Science and Technology*, Athens, Greece, 1994, 331–346.
94. V. D. McGinniss, *Paint Coatings Ind.* **10**(7), 34–39 (1994).

General References

95. *Proceedings of Radcure 84 Conference*, Atlanta, Ga., published by the Association for Finishing Processes of SME, Dearborn, Mich., 1984.
96. *Proceedings of Radcure 86 Conference*, Baltimore, Md., published by Association for Finishing Processes of SME, Dearborn, Mich., 1986.
97. *Proceedings of RadTech 88 North American Conference*, New Orleans, La., published by RadTech International, Northbrook, Ill., 1988.
98. *Proceedings of RadTech 90 North American Conference*, Vols. 1 and 2, Chicago, Ill., published by RadTech International, Northbrook, Ill., 1990.
99. *Proceedings of RadTech 92 North American Conference*, Vols. 1 and 2, Boston, Mass., published by RadTech International North America, Northbrook, Ill., 1992.
100. *Proceedings of RadTech 94 North American Conference*, Vols. 1 and 2, Orlando, Fla., published by RadTech International North American, Northbrook, Ill., 1994.
101. Suppliers of radiation-curable materials: CIBA-GEIGY (photoinitiators), Aceto Corp. (photoinitiators), BASF (photoinitiators), Henkel (photoinitiators), Sartomer (monomers, cross-linking agents/oligomers, polymers), Henkel (cross-linking agents/oligomers, polymers), Cargill (polymers).

VINCENT D. MCGINNISS
Battelle Columbus Laboratory

Related Articles

Lithographic resists; Insulation, electric wire and able coverings; Microwave technology; Infrared technology; Plasma technology; Photochemical technology