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Radiation Curing of Inks and Coatings

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
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Washington, DC 20234

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ABSTRACT

The science and technology of curing organic materials with radiation is reviewed. Electron beam, ultraviolet, infrared, microwave, and high frequency radiation sources and the resin systems suitable for use with these sources are considered. Equipment necessary to affect a radiation cure is discussed and some practical problems unique to each radiation method are indicated. The application of radiation curing to industrial processes which employ inks and coatings is covered, with particular emphasis given to printing with radiation curable formulations. Included are discussions of the advantages and disadvantages of radiation cured inks, some typical ink components and formulations, the specialized machinery required, and the influence of parameters unique to radiation curing methods on the printing process. Other nonprinting but related industrial operations utilizing radiation for treating thin films and coatings are also considered. Some costs, examples, and market statistics are given for these commercial procedures. Newer nonconventional, but also nonradiation, alternative curing methods are discussed briefly. A bibliography of recommended further reading and a list of over two hundred fifty references are included.

CONTENTS

I PURPOSE, SCOPE, AND SUMMARY OF THE REPORT

The purpose of this report is to survey the open literature on the radiation curing methods using inks primarily, but also other coatings, as a background for further research. Newer nonradiation methods and applications of radiation to fields other than coatings will also be considered briefly.

The science and technology of curing organic materials with radiation is the subject of the first part of the report, Chapters II through VI. The opening section is primarily introductory in nature and encompasses a definition of the curing process, the motivations for exploiting solventless curing with radiation, the basic principles of the interaction of various forms of radiation with matter, and a kinetic scheme for polymerization and oxidation, chain reactions which can be initiated by molecular species excited by the aforementioned interactions.

The following two chapters, III and IV, consider the most common radiation sources used to induce curing reactions: electron beams (EB) and ultraviolet (UV) light. The transfer of energy from electrons to molecules to form excited species and an indication of possible reactions that these excited molecules may undergo is outlined for materials subjected to EB bombardment. Since the energy imparted by UV radiation is much less than for EB, special excitable molecules referred to as photoinitiators or photosensitizers must be added to insure that exposure to UV light yields the desired chemically reactive species. The six major groups of these compounds are detailed, with examples of each type provided. The equipment necessary to affect a radiation cure is discussed and some practical problems unique to each of these radiation methods are indicated for both EB and UV curing systems.

Since the resin-forming chemical substances employed for EB and UV radiation curing are often identical, mention of these materials is not made in either of the preceding two sections but instead is the topic of Chapter V. The three common types of oligomers or reactive short-chain polymers, namely cationic, thiol-ene, and acrylic, are considered in detail, as are monomers or reactive diluents. Some examples of the usage of these and other constituents in typical coating formulations are presented.

The final discussion of curing promoted by radiation is that of infrared (IR), microwave, and high frequency curing. It has been estimated that of all the radiation curing methods, IR has the broadest potential for use although, at present, EB and UV are exploited commercially to a much greater extent. The mechanisms of curing, typical equipment required, and some special problems are considered for these methods, however in less detail than in the earlier chapters covering EB and UV sources.

The application of radiation curing to industrial processes that employ inks and coatings is covered in the second part of the report, Chapters VII through X. First to be discussed are the large-scale processes of roll, curtain, and spray coating, all of which have been used to apply radiation curable formulations. Following this, Chapter VIII gives details on printing with EB and UV curable inks. Included are a brief summary of the common printing methods, e.g., typography, planography, intaglio, and silkscreen, a presentation on the advantages and disadvantages of radiation cured inks, an outline of typical ink components and formulations, and an indication of the specialized machinery required. The influence of some parameters unique to radiation curing methods on the printing process is also considered.

Other nonprinting industrial procedures utilizing radiation or radiation curing, some for treating thin films and coatings, are illustrated in a separate section. These include such diverse commercial areas as crosslinking wire insulation, rubber tires, and dental fillings, preparation of resists for microelectronic device fabrication, and sterilizing medical supplies. The final chapter in this part gives some costs, examples, and market statistics for the industrial usage of both radiation curing in general and for radiation cured printing inks.

The report concludes with a chapter on newer nonradiation curing methods, presenting a short discussion on modified heatset, high solids, surface coated, and water-based inks, catalytic two part coatings, electro-deposited coatings, and jet printing; all materials or techniques which are alternatives to both conventional and radiation curing. A bibliography of recommended references giving more detailed expositions on a number of the topics covered in this report is included for further background reading and can be found in Chapter XIII.

II INTRODUCTION TO RADIATION CURING

Printing inks, paints, and other coatings are applied as a liquid or paste but must change to a solid and nontacky state before the painted or coated article can be used. The change is known as curing or drying. Sometimes it occurs by physical means, the evaporation of a solvent or dispersion medium for example, and sometimes by chemical changes such as polymerization and crosslinking. These chemical processes connect the many relatively small molecules of the original liquid or paste into a large molecular network or insoluble solid, which may be either rigid or rubbery in consistency depending upon the requirements of a particular application. Among traditional materials, gravure inks and many lacquers dry by solvent evaporation while paints and inks based upon linseed oil "dry" by chemical crosslinking promoted by oxygen in the air. Considerable time is usually required for curing in both methods and the evaporation of solvents can result in air pollution and potential fire hazards. There is also a tendency of the media to dry upon presses, brushes, sprayers, and other application equipment. The long cure time requirement raises difficulties in modern production lines; the other factors have become more acute since the rapid rise of petroleum prices and the advent of air pollution legislation.

A variety of new curing systems have been devised to avoid or cope with these difficulties. Many are somewhat alike for inks and coatings. In particular, methods using radiation have proliferated. "Radiation" has been given at least three distinct meanings in various contexts: (a) broadly, all energy traveling as electromagnetic waves or active particles such as electrons and ions, (b) more narrowly, waves or particles whose elementary units carry enough energy to break chemical bonds and cause chemical reaction directly, quite aside from any heating effect, (c) ionizing radiation, or that having energy much greater than visible or ultraviolet. A survey of the electromagnetic spectrum relating the energy, frequency, ν, and wavelength, λ, of various types of radiation is shown in Table 1 [1].

The carriers of radiation, e.g. photons, electrons, or ions, are initially at high speed or of high kinetic energy, and when they pass near to or collide with molecules of a target material they can cause

TABLE 1

The Wavelength, Frequency, and Energy for Various Types of Electromagnetic Radiation

Wavelength λ, nm	Frequency ν, s^{-1}	Energy, eV	Source and/or Type
1.25×10^{-5}	2.4×10^{22}	9.9×10^{7}	hard x-rays
1.0×10^{-4}	3.0×10^{21}	1.2×10^{7}	high energy γ-ray limit
6.0×10^{-4}	5.0×10^{20}	2.1×10^{6}	Y^{90} β electrons
4.0×10^{-3}	7.5×10^{19}	3.1×10^{5}	Co^{60} β electrons
1.25×10^{-2}	2.4×10^{19}	9.9×10^{4}	high energy soft x-ray limit
2.5×10^{-2}	1.2×10^{19}	5.0×10^{4}	low energy γ-ray limit
6.8×10^{-2}	4.4×10^{18}	1.8×10^{4}	H^{3} β electrons
1.25×10^{-1}	2.4×10^{18}	9.9×10^{3}	low energy soft x-ray limit
2.0×10^{-1}	1.5×10^{18}	6.2×10^{3}	vacuum UV range
1.8×10^{2}	1.7×10^{15}	6.9	
2.0×10^{2}	1.5×10^{15}	6.2	short wave UV limit
2.54×10^{2}	1.2×10^{15}	4.9	low pressure Hg lamp
4.0×10^{2}	7.5×10^{14}	3.1	long wave UV limit
4.2×10^{2}	7.1×10^{14}	3.0	visible (violet)
6.8×10^{2}	4.4×10^{14}	1.8	visible (red)
7.0×10^{2}	4.3×10^{14}	1.7	short wave IR range
2.0×10^{3}	1.5×10^{14}	6.2×10^{-1}	medium wave IR range
4.0×10^{3}	7.5×10^{13}	3.1×10^{-1}	long wave IR range
1.0×10^{6}	3.0×10^{11}	1.2×10^{-3}	
3.3×10^{6}	9.1×10^{10}	3.8×10^{-4}	short wave microwave limit
1.4×10^{7}	2.1×10^{10}	8.9×10^{-5}	K band wavelength center

TABLE 1 (continued)

Wavelength λ, nm	Frequency ν, s^{-1}	Energy, eV	Source and/or Type
3.0×10^{7}	1.0×10^{10}	4.1×10^{-5}	X band wavelength center
1.5×10^{8}	2.0×10^{9}	8.3×10^{-6}	LS band wavelength center
2.7×10^{8}	1.1×10^{9}	4.6×10^{-6}	long wave microwave limit
3.0×10^{8}	1.0×10^{9}	4.1×10^{-6}	UHF range
1.0×10^{9}	3.0×10^{8}	1.2×10^{-6}	VHF range
1.0×10^{10}	3.0×10^{7}	1.2×10^{-7}	

Source: After J. Lacey, A. H. Keough, "Radiation Curing, A Discussion of Advantages, Features, and Applications," Assoc. Finishing Processes Soc. Manuf. Engrs., Dearborn, MI, 1980, p. 13.

ionization, excitation to higher energy states, or fragmentation of the target, the carriers losing energy in the process. The molecular processes that can be brought about directly by absorbed radiant energy are governed by the size of the atomic packet of energy, E, of the radiation, calculated from the equations:

$$E = h\nu \text{ or } E = ch/\lambda$$

where h is Planck's constant and c the speed of light. Photons will be absorbed by a substance with a probability that varies with the strength of the absorption spectrum at the wavelength involved. The act of absorption excites the molecule to a state of higher energy. This excited molecule may do several things: (a) re-radiate all or a part of the energy, (b) transfer it to other nearby molecules by a radiationless transition, thus going back to the original state or some other state of lower energy than the excited state, or (c) break into fragments or enter into other chemical reactions. Usual energies required to break a chemical bond are in the range from 125 to 500 kJ/mol (30 to 120 kcal/mol). A few typical values are given in Table 2 [2,3]. In many instances, much of the absorbed energy will ultimately appear as heat. Radiation of photon energy too low to break chemical bonds can still bring about reaction indirectly by raising the temperature of the absorbing medium and thus accelerating a normal thermal reaction. Thus, electromagnetic radiation with E on the order of or greater than 1.5 eV (125 kJ), corresponding to wavelengths lower than 953 nm, i.e. visible, ultraviolet (UV), x-rays, and gamma-rays, can bring about reaction by direct photochemical action, while the other lower energy kinds, especially microwave and most infrared (IR), are merely devices for heating.

TABLE 2

Energies of Some Common Covalent Bonds at 298 K

Bond	Molecule	Bond Energy, kJ/mol	eV
H-H	H_2	436	4.52
C-H	Paraffins	385-435	3.99-4.51
	Olefins	≥ 452	≥ 4.69
	Acetylene	523	5.43
	Benzene	461	4.78
$t\text{-}C_4H_9\text{-}H$	$i\text{-}C_4H_{10}$	385	3.99
$PhCH_2\text{-}H$	Toluene	356	3.69
RCO-H	Aldehydes	360-366	3.73-3.80
C-C	Ethane	368	3.82
$PhCH_2\text{-}CH_2R$	Propylbenzene, Butylbenzene	280-289	2.90-3.00
RCO-COR	Biacetyl, Benzil	278-282	2.88-2.93
C=C	Ethylene	720	7.47
C≡C	Acetylene	962	9.98
C-O	Aryl alkyl ethers	239-280	2.48-2.90
C=O	CO_2	532	5.52
C≡O	CO	1076	11.16
C-N	Amines	255-300	2.65-3.11
O-H	H_2O	498	5.17
	Alcohols	428-439	4.44-4.55
O-O	H_2O_2	213	2.21
	Alkyl peroxides	152-159	1.58-1.65
	Acyl peroxides	127	1.32
O=O	O_2	498	5.17
S-H	H_2S	377	3.91
S-S	S_2	425	4.41
S=O	SO_2	552	5.73
N-H	NH_3, amines	310-460	3.22-4.77
N≡N	N_2	945	9.80

TABLE 2 (continued)

Bond	Molecule	Bond Energy, kJ/mol	eV
F-F	F_2	157	1.63
Cl-Cl	Cl_2	243	2.52
Br-Br	Br_2	194	2.01
I-I	I_2	153	1.59
C-F	CH_3F	452	4.69
C-Cl	CCl_4	295	3.06
C-Br	CH_3Br	293	3.04
C-I	CH_3I	236	2.45

Source: "CRC Handbook of Chemistry and Physics," R. C. Weast, Ed., 63rd Ed., CRC Press, Boca Raton, FL, 1982, pp. F185-F202.

There are important differences between the effects of radiation induced photochemical processes in the visible and UV, which usually involve absorption of a photon in specific chemical bond systems having a suitable absorption spectrum, and the action of very high energy radiation such as gamma rays and electrons. Although there are various mechanisms for absorption of ionizing radiation in matter, there is a strong tendency for the absorption of both electrons and gamma rays to be nonspecific and roughly proportional to the density of the material traversed. High energy radiation is more penetrating than low energy radiation of the same kind, and for the same energy, gamma rays are much more penetrating than electrons. It is thought that the primary action of gamma and other forms of high energy radiation is to liberate electrons, so the chemical effect is much like that of irradiation with an electron beam (EB). The lowest energy x-rays are an exception to this generalization in that their absorption can be strong for specific kinds of atoms.

Many important photochemical or radiation induced processes occur by a chain reaction mechanism. One primary photochemical or radiation induced chemical reaction, initiation, produces reactive atoms, free radicals, or ions which start a long sequence of spontaneously occurring reactions, or propagation. This is especially so with polymerization and oxidation, as indicated schematically below:

<u>Polymerization</u>

$C + h\nu \xrightarrow{k_1} 2R\cdot$ Initiation

$R_i\cdot + M \xrightarrow{k_2} R_{i+1}\cdot$ Propagation

$R_i\cdot + R_j\cdot \xrightarrow{k_4} P_{i+j}$ Termination

Oxidation

$$C + h\nu \longrightarrow 2R\cdot \qquad \text{Initiation}$$

$$\left.\begin{array}{l} R\cdot + O_2 \longrightarrow RO_2\cdot \\ RO_2\cdot + RH \longrightarrow ROOH + R\cdot \end{array}\right\} \text{Propagation}$$

$$\left.\begin{array}{l} R\cdot + RO_2\cdot \longrightarrow ROOR \\ R\cdot + R\cdot \longrightarrow RR \\ RO_2\cdot + RO_2\cdot \longrightarrow \text{Products} \end{array}\right\} \text{Termination}$$

In these equations C is an initiator molecule, R· a free radical species, M a monomer molecule or chain unit, $R_i\cdot$ a free radical with i monomer units in the chain, P_i a polymer molecule containing i monomer units, and R (without dot) a part of a molecule.

Although the number of primary acts, such as initiation, is often proportional to the total number of quanta or electrons absorbed irrespective of the intensity or time-rate of absorption, the total amount of chain reaction varies in a more complicated way. Thus, at steady state:

$$\frac{d[R\cdot]}{dt} = k_1 I[C] - k_4[R\cdot]^2 = 0$$

$$[R\cdot] = \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [C]^{\frac{1}{2}}(I)^{\frac{1}{2}}$$

$$\frac{d[M]}{dt} = -k_2[R\cdot][M] = -k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [C]^{\frac{1}{2}}(I)^{\frac{1}{2}}$$

where I is the intensity of radiant illumination and the brackets denote concentration of the appropriate chemical species. It is apparent from the final equation that the rate of consumption of monomer, which is equivalent to the rate of production of polymer, is proportional to the one-half power of both initiator concentration and light intensity. Since the consumption of initiator and light is proportional to I[C] and conversion of monomer only to $\{I[C]\}^{\frac{1}{2}}$, it is evident that the efficiency of utilization of both initiator and light falls off at high intensities:

$$\frac{-d[M]/dt}{d[C]/dt} \quad \alpha \quad \frac{\{I[C]\}^{\frac{1}{2}}}{I[C]} = \{I[C]\}^{-\frac{1}{2}}$$

These same arguments apply to initiation by ionizing radiation except that no initiator is needed. Although gamma radiation has been used in some polymer applications where very deep penetration is essential (sterilization, wood and concrete impregnation), the industrial use of chemically active radiation for coatings and inks has been restricted to EB and UV, as will be discussed in a later section of the report.

Although, in principle, coatings might be applied as monomers and simply polymerized to a cured product, the composition of radiation cured coatings and inks has evolved differently. Most common monomers are too fluid and too volatile for application as a coating; moreover, they do not utilize the radiation with the greatest possible efficiency. Therefore, considerably larger molecules containing some reactive sites--oligomers or prepolymers--are used instead as the main component. In this way only a few additional reactions need occur to make a large polymer molecule. However, a certain amount of a monomer is also present to bring about the appropriate application viscosity combined with the most efficient curing. Peroxide cured compositions of this general character, consisting of unsaturated polyester and styrene, have had a long record of successful use in wood coating and fiber-glass composite production and the early experiments with radiation curing began with them. It was soon realized that oligomers and monomers containing acrylic ester groups were much faster curing than the styrene and unsaturated polyester system and that monomer constituents bearing several reactive functional groups, such as the example trimethylolpropane triacrylate shown in Figure 1, were also faster curing than monofunctional acrylates. Two nonacrylate systems are also competitive in the coatings field, the thiol-ene system and the cationic photoinitiator system, but the overwhelming majority are acrylic based.

Current ionizing radiation and UV cured coating and ink systems usually contain the following components:

- oligomer
- monomer
- pigment (absent in clear coatings)
- initiator (absent in EB cured materials)
- minor additives (inhibitors to prevent polymerization in storage, pigment dispersion aids, etc.)

These systems are such that, in theory, there need be no polymerization on the handling equipment but only on the coated object after exposure to radiation. Furthermore, unlike most thermally promoted initiators, the radiation-sensitive initiators can react at room temperature without additional heating and the irradiating power of present machines is such that cure is completed in a very short time. Finally, the monomer, which serves partially as a thinner during application, is converted to solid resin and, therefore, air pollution by evaporated solvent is not a problem. These features combine to make possible a considerable

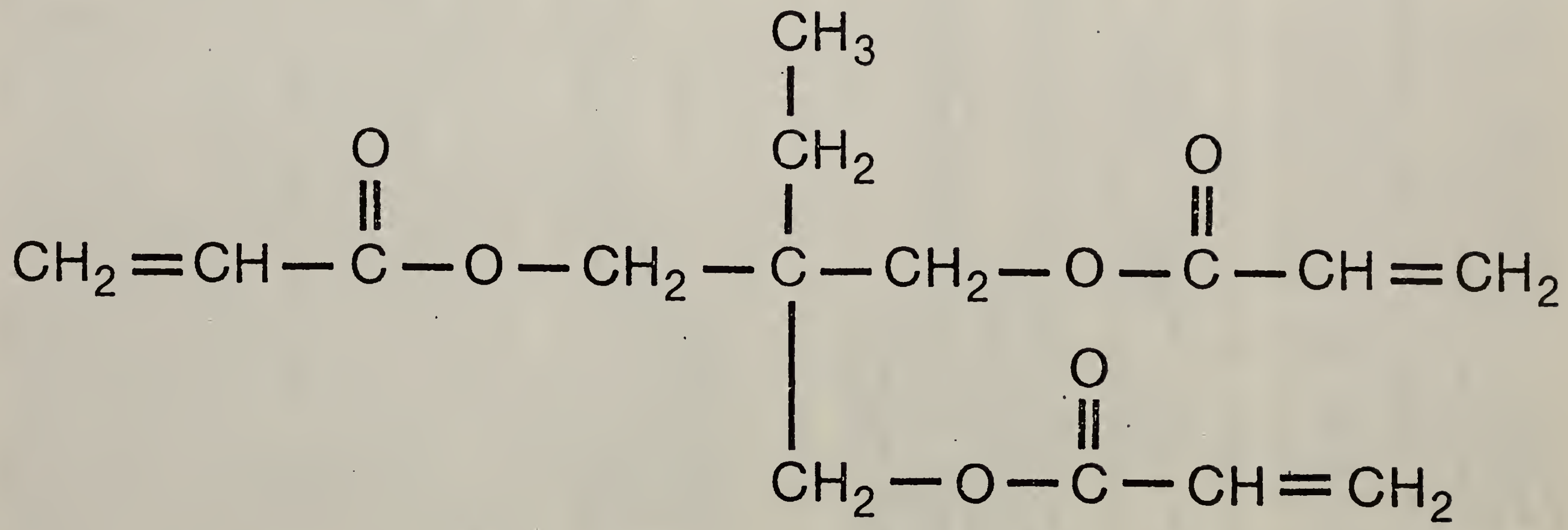


FIGURE 1 The multifunctional acrylic monomer trimethylolpropane triacrylate.

savings in equipment cleaning, time, heating requirements, and in solvent recovery or incineration systems. Countering these advantages is the greater cost of materials and equipment needed for radiation curing.

III ELECTRON BEAM CURING-PRINCIPLES AND MACHINERY

A Energy Deposition by Electrons

To cause chemical reactions, the energy of fast electrons must be transferred to the molecules of the material irradiated. This happens in small steps and with many changes in the direction of an electron. A simple rule is that the probability of an inelastic collision for a fast electron varies with the inverse square of its velocity [4]. Application of this rule is complicated greatly by scattering of electrons in the target and by the requirement that the relativistic mass must be used at the high electron energies encountered. This mass is not a constant but depends on electron velocity and is typically increased many-fold over its normal constant value, as required by the principles of relativity theory. Figures 2, 3, and 4 [5,6] give an accurate description, calculated from theoretical models, of how the energy deposition rate varies with depth for electrons penetrating into thicknesses of polymeric materials, and Figure 5 shows the limiting penetration (the x-intercepts from Figure 2) as a function of initial electron energy [7]. Most of the energetic interaction is with the electrons of the penetrated material. Since the number of electrons in an atom is roughly proportional to its relative atomic mass, absorption per unit distance traversed tends to be proportional to density. Therefore, the thickness to be irradiated is often given instead as the product of thickness and density, $t\rho$, in units of mg/cm^2 or g/cm^2.

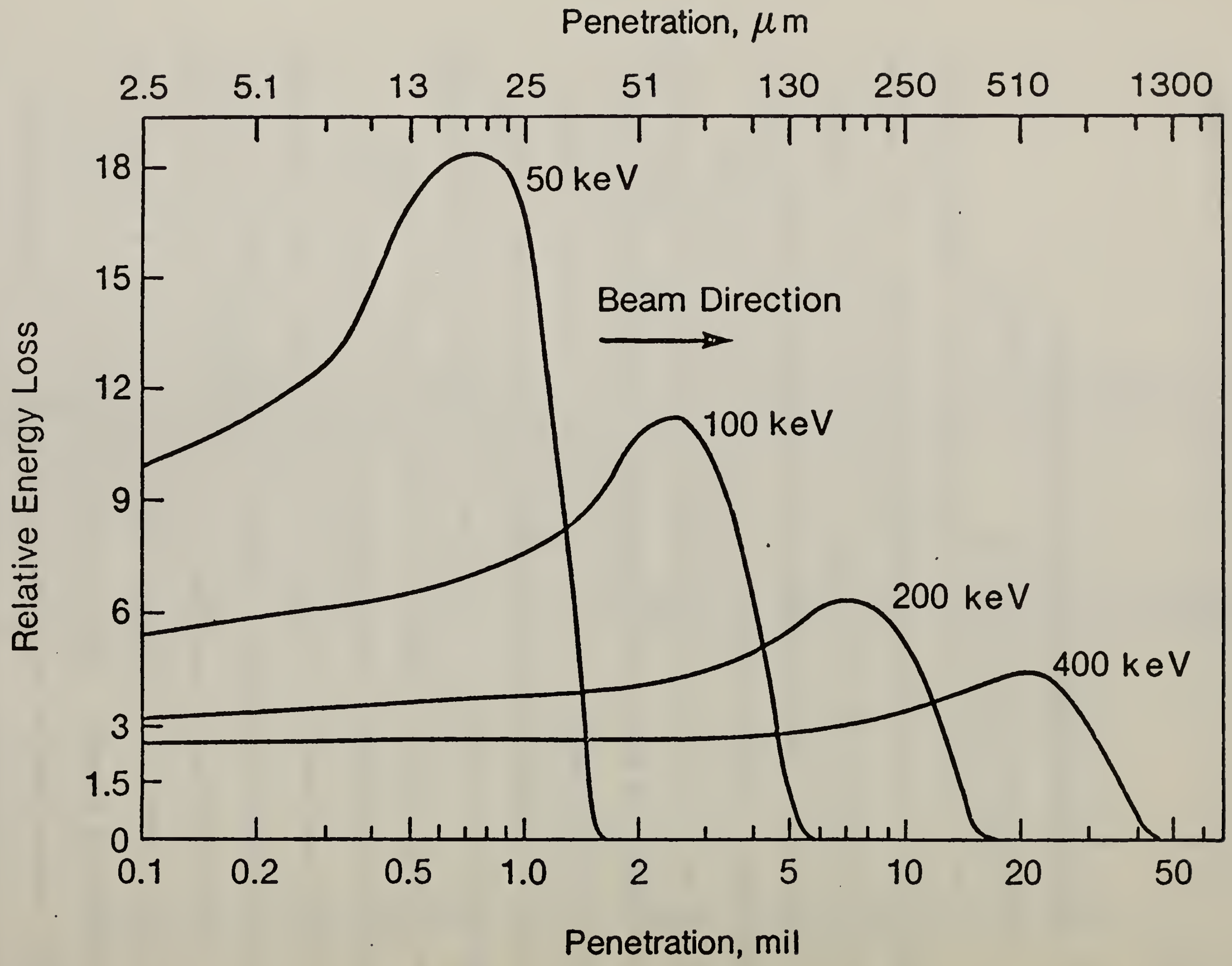
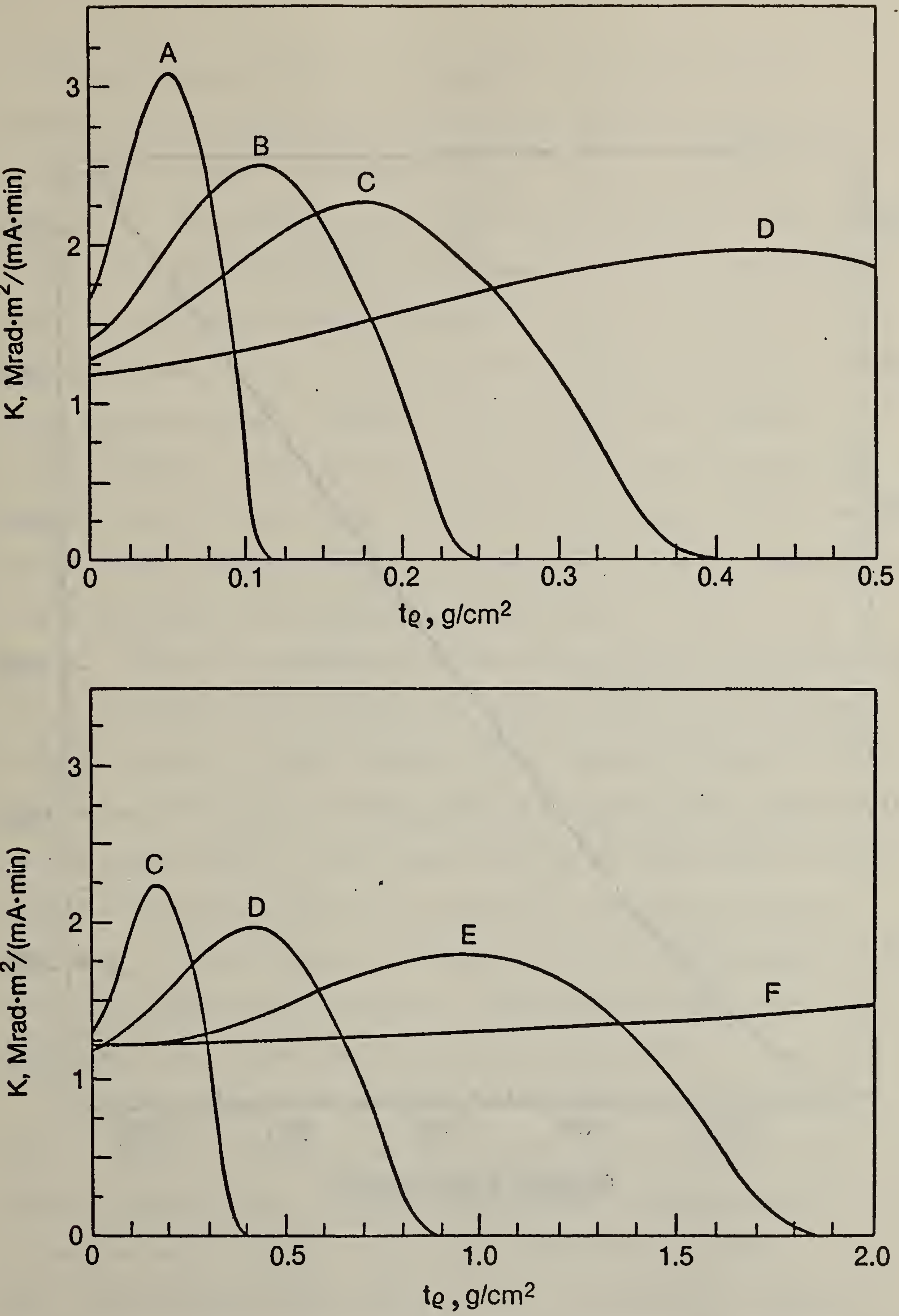


FIGURE 2 Depth-dose distribution curves for polystyrene in the low energy range .



FIGURES 3 and 4 Depth-dose distribution curves for polyethylene or water (after passage through 40 μm titanium window and 10 cm air; high energy range). Ordinates are energy deposition rate as Becker-Bly area processing coefficient K. Electron energy, MeV: A, 0.4; B, 0.7; C, 1.0; D, 2.0; E, 4.0; F, 10.0.

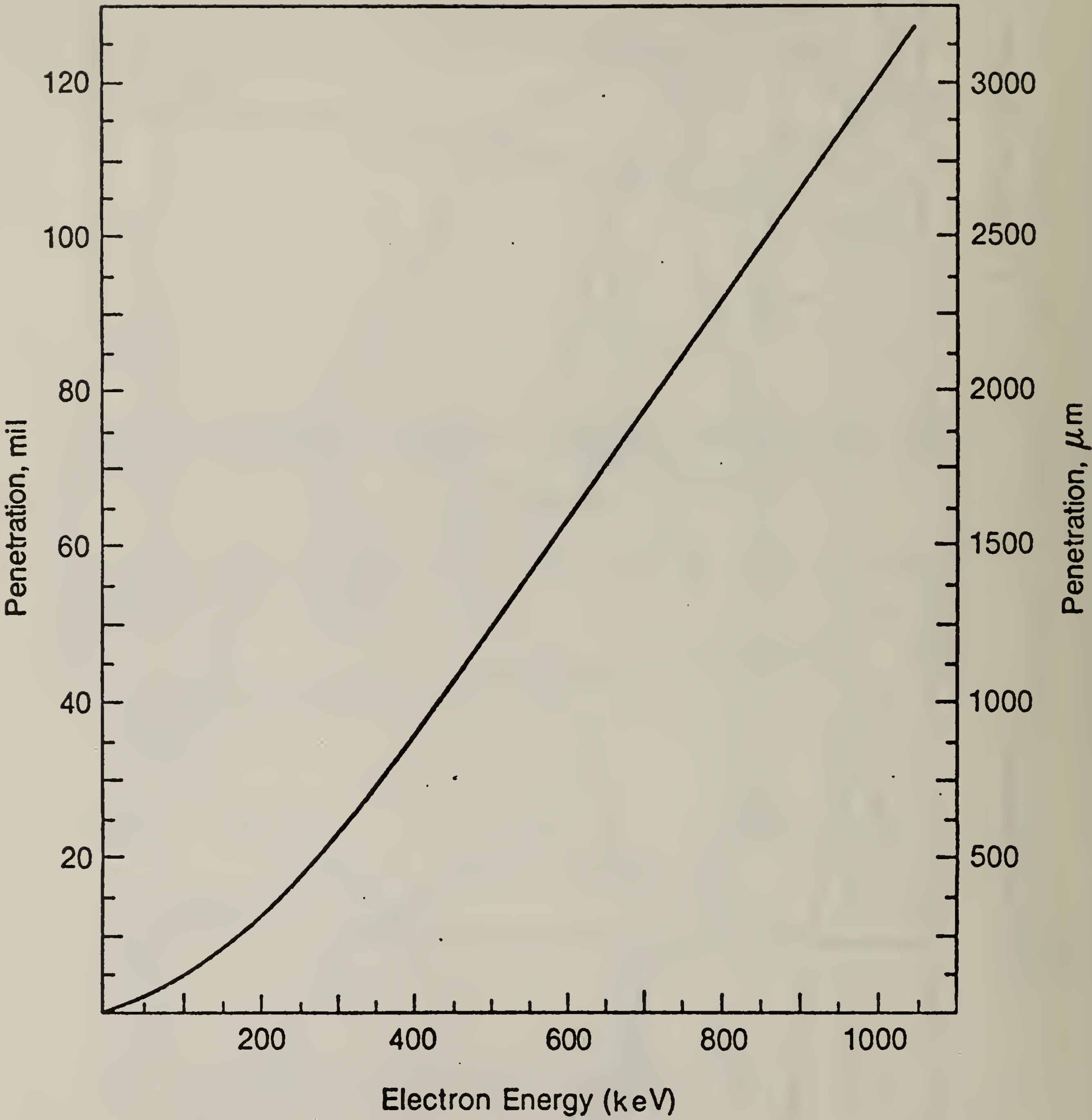


FIGURE 5 Penetration as a function of energy for electrons in polystyrene.

The outstanding exception to the general rule stated above is hydrogen, which is about twice as rich in electrons per unit mass as the elements of higher relative atomic mass. This fact accounts for a large part of the dependence of the optimal $t\rho$ upon material composition for organic substances with varying hydrogen contents, as illustrated in Table 3. The thickness values [6] given in Table 3 are related to the penetration range of electrons in the materials shown in Figure 5 but are smaller because allowance is made in the table for the following two practical factors. First, a portion of the electron path is through the window and the air space between the window and the sample, which dissipates otherwise useful electron energy. The second factor involves the objective of an approximately uniform exposure for curing in all layers of the coating. This can be achieved at the far end of the sample, where the rate of energy deposition has fallen to perhaps fifty to sixty percent of the surface rate, by using excess electron energy at the expense of allowing some of the beam to escape into the substrate, thereby wasting the beam energy remaining. Low energy electrons are advantageous for thin coatings because they conform with requirement two above, but on the other hand, a larger fraction of the total energy is consumed passing through the window and the air layer. Matters such as these are discussed systematically and in more detail by several authors [5-7].

The energy absorbed per unit mass is called the dose; customary units are the rad, 10 millijoules per kilogram, and its multiple the megarad. The most recent work sometimes uses the SI recommended unit for absorbed dose, the gray. Table 4 gives definitions of units, terms, and conversion factors commonly used in discussions of radiation curing [6,8]. One unit deserves some special explanation. The yield

TABLE 3

Optimum Product Thickness for Electron Beam Irradiation of Several Organic Materials

Electron Energy, MeV	Optimum Value of Thickness Density Product[a], g/cm^2 Polyethylene	Polystyrene	Carbon
0.3	0.019	0.020	0.022
0.4	0.051	0.054	0.059
0.5	0.085	0.090	0.098
0.6	0.119	0.127	0.138
0.8	0.190	0.203	0.220
1.0	0.263	0.278	0.302
1.5	0.449	0.475	0.517
2.0	0.634	0.671	0.733
3.0	1.02	1.08	1.18
4.0	1.40	1.48	1.61
5.0	1.77	1.88	2.04
10.0	3.68	3.90	4.24

[a] Value given is $t\rho_{opt}$ for equal entrance and exit doses, adjusted for beam window and air layer (40 μm Ti and 10 cm air).

Source: R. C. Becker, J. H. Bly, M. R. Cleland, J. P. Farrell, Radiat. Phys. Chem. 14, 353 (1975).

TABLE 4

Definition of Terms, Units, and Conversion Factors Used in Radiation Curing

---

dose = Amount of energy absorbed per unit mass; e.g. gray, rad

gray (Gy) = Unit of dose, equal to absorption of one joule per kilogram (J/kg)

rad (rd) = 0.01 gray = 100 erg/g

dose rate = Dose per unit time; e.g. gray or rad per second

energy (joule) = $h \cdot \nu$ = (Planck constant, 6.626×10^{-34} J·s)·(frequency, s^{-1}) = $h \cdot c/\lambda$ = h·(velocity of light, 3.0×10^{8} m/s)/(wavelength, m)

eV = Electron volt, unit of energy equivalent to the kinetic energy acquired by an electron accelerated across a potential of one volt

ϕ = Quantum yield, number of atoms or molecules undergoing a particular process per quantum of absorbed radiation

G-value = Energy yield (akin to ϕ), number of atoms or molecules undergoing a particular process per 100 eV absorbed energy

K = Becker et al. area processing coefficient used to relate dose, conveyor width, beam current, and conveyor speed as follows:

$$\text{dose, Mrad} = \frac{K \cdot (\text{current, mA})}{(\text{width, m}) \cdot (\text{speed, m/min})}$$

1 angstrom (Å) = 10^{-8} cm = 10^{-4} micrometer (μm) = 10^{-1} nanometer (nm)

1 megarad (Mrad) = 10^{6} rad = 10^{4} gray = 10 watt·s/g = 6.25×10^{19} eV/g

1 MeV = 10^{6} eV = 1.6×10^{-13} J = 9.6×10^{7} kJ/mol = 1.6×10^{-6} erg

1 watt (W) = J/s = Gy·kg/s = 10^{5} rad·g/s = 10^{7} erg/s

Source: After J. Lacey, A. H. Keough, "Radiation Curing, A Discussion of Advantages, Features, and Applications," Assoc. Finishing Processes Soc. Manuf. Engrs., Dearborn, MI, 1980, p. 13.

of any chemical process or species is stated as the G-value, i.e., atoms or molecules per 100 eV absorbed energy. The G-values for primary processes range from a small fraction of a unit to several units; a G-value of about fifteen would correspond to nearly total efficiency in breaking very strong chemical bonds of about 7 eV and is rarely achieved. On the other hand, G-values for chain reactions can range in the hundreds or thousands depending on the chain kinetics. A few typical G-values for various chemical processes or products are shown in Table 5 [9].

As an example of how the preceding information is typically used, processors knowing the layer thickness to be irradiated and the desired dose can determine the accelerating voltage needed from the thickness of the material to be penetrated (see Table 3 for example). They would then use conveyor speeds and beam currents satisfying the area processing coefficient equation, found at the end of Table 4. Many coatings have now been developed to cure adequately with doses of the order of 1 Mrad. It is fortunate that this is so, at least for work with paper substrates, since much higher doses damage the substrate profoundly. For example, 10 Mrad totally destroyed the folding endurance of banknote paper [10,11].

B Commercial EB Curing Machinery

Although UV today has a larger share of the market, ionizing radiation developed earlier as a source of initiation. The important commercial sources of ionizing radiation are gamma rays (mostly from cobalt 60) and EB machines. The latter are much more powerful and have the advantage that they can be turned off when not in use. In operation, electrons are emitted from a heated filament in an evacuated chamber, accelerated and deflected by electrostatic and electromagnetic fields, and finally allowed to escape from the vacuum tube through a thin foil

TABLE 5

G-Values for Radiation Processes or Products

n-Heptane, liq., consumed	$G(-C_7H_{16})$	=	6.8
n-Heptane, liq., H_2 produced	$G(H_2)$	=	4.2, 3.9
n-Heptane, liq.	$G(CH_4)$	=	0.09
n-Heptane, liq.	$G(C_2H_4)$	=	0.18
n-Heptane, liq.	$G(C_2H_6)$	=	0.25
n-Octane, radicals by iodine uptake	$G(-I_2)$	=	3.3, 4.3
n-Paraffins, dimers	G(dimer)	=	3 - 5
Benzene, radicals by iodine uptake	$G(-I_2)$	=	0.66
Toluene, radicals by iodine uptake	$G(-I_2)$	=	2.4
Acetic acid	$G(H_2)$	=	0.9
Acetic acid	G(CO)	=	0.5
Acetic acid	$G(CO_2)$	=	2.8
Polystyrene	G(crosslinks)	=	0.05
Poly(methyl methacrylate) 25 °C	G(scissions)	=	1.23
Cellulose	G(scissions)	=	10
Methyl acrylate[a]	G(main chain units)	=	600
Styrene[a]	G(main chain units)	=	1000
Methyl methacrylate[a]	G(main chain units)	=	2000
Acrylonitrile[a]	G(main chain units)	=	40000

[a] Expected to be highly dependent upon dose rate and other conditions.

Source: A. Charlesby, "Atomic Radiation and Polymers," Pergamon, New York, 1960, pp. 186-190, 295, 343, 362, and 388.

window. Two types are in use: (a) the scanned beam machines, in which the electrons are generated nearly as a point source and the narrow beam scanned electromagnetically over the desired area, as in a television tube, and (b) the linear-filament type or curtain processor, in which electrons are emitted from a line-source filament, which can be up to a meter or more in length, and are accelerated perpendicular to the filament in a continuous linear curtain. Figure 6 shows the two types diagrammatically [5]. The former type, of which there are several subclasses, can produce electrons of low or high energy, up to several MeV. The linear filament models are restricted to low energies, on the order of 350 keV or less. In industrial curing, the work to be processed is carried past the window of the electron machine on a conveyor. If a scanning model is used, the scanning rate is so much more rapid than the conveyor speed that practically uniform coverage results. The energy consumed by EB curing is especially low, sometimes estimated as one-tenth that of UV curing, which is in turn less than that of any kind of gas heating [12].

EB machines of the scanning type have been made by High Voltage Engineering Corporation[*] in the kilovolt and megavolt range of accelerating potential, with powers up to 100 kW and beam current levels of 100 to 200 milliamperes. Costs in 1979 had decreased to \$3000 to \$5000 per kilowatt output for high voltage equipment and to about \$1500 per milliampere for low-voltage (150 to 300 keV) equipment [13]. Scanning high voltage machines to 200 kW at 4 MeV and 100 kW at 5 MeV are made by Radiation Dynamics, Incorporated (a subsidiary of the Monsanto Co.)

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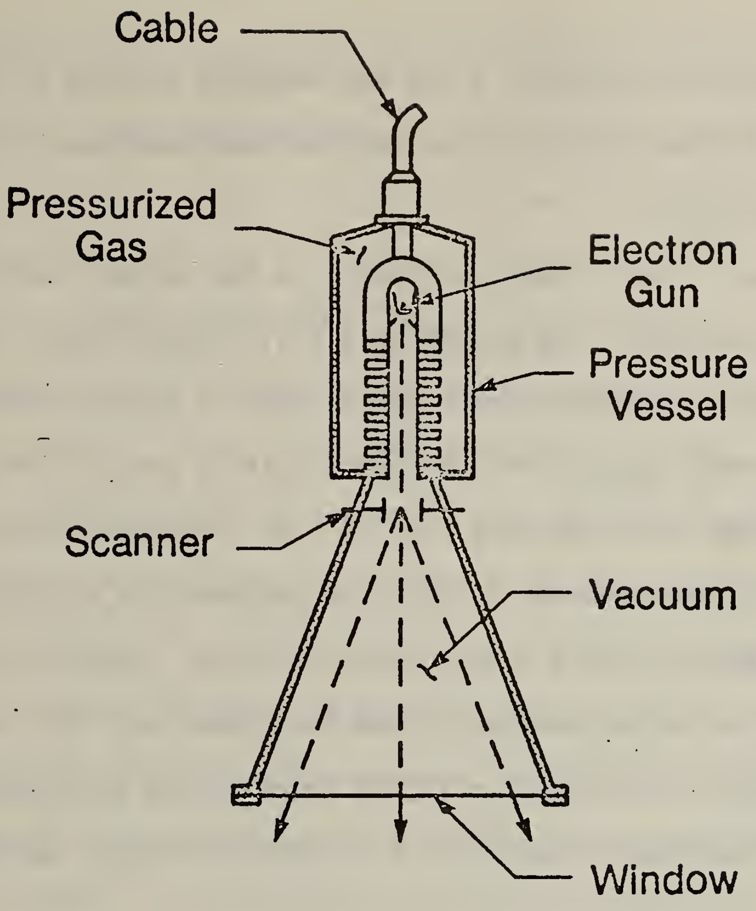
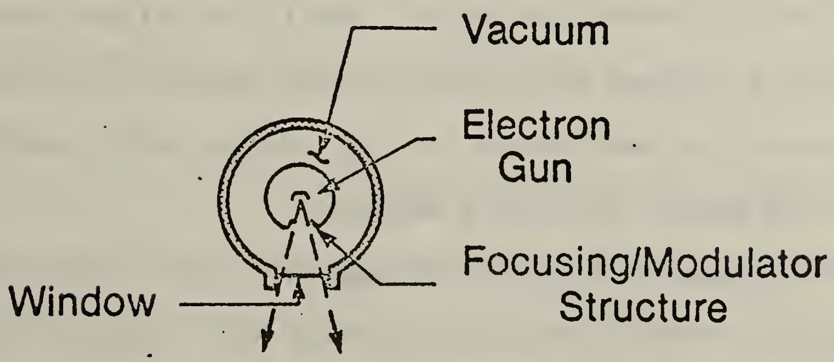
[*] Certain commercial equipment, instruments, or materials are identified in this report. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.



(a) Conventional Hybrid System



(b) Curtain Processor

FIGURE 6 Two electron beam source types currently available.

under the name Dynamitron [14]. A 150 keV scanning machine with a remarkably thin window, 12.5 μm titanium, has been developed in Germany by Polymer Physik [15].

The principal linear electrode machine in the United States is the Electrocurtain, available from Energy Sciences, Incorporated. A production line 122 cm wide has been described as well as pilot plant equipment for laminating, coating, and ink application with a width of 46 cm and speeds ranging from 10 to 500 cm/s [16,17]. At 1 Mrad applied dose, a line speed of 250 cm/s requires a source output power of 60 W/cm (2.7 kW in a 46 cm wide machine) at a beam current of 18 mA. Details have recently been given on maintenance of the Electrocurtain; for example, filament life may be from 3,000 to 10,000 hours before replacement [18]. Somewhat similar machines, e.g. T.I.G.E.R. [19], have been developed in England.

C A Few Special EB Curing Problems

EB machines require considerable shielding. Although electrons are readily stopped, the x-rays produced by their collisions with matter are much more penetrating. Small, low voltage machines are sold as complete packages with lead shielding included. The shielding requirements are more severe for high voltage units where concrete, earth, and gravel are usually employed.

The passage of electrons through air produces appreciable ozone, which is a powerful curing inhibitor for most coating compositions and also a potential health hazard. Therefore, an inert atmosphere is usually employed in the vicinity of irradiation. Although nitrogen can be used, large installations instead often generate an inert gas blanket by burning methane with slightly less than the stoichiometric amount of air needed for complete combustion [20]. The common use of inert atmospheres in EB applications obviates any difficulty with the inhibition of curing by oxygen, which can occur in UV initiated processes.

Pigments can cause severe limitations in UV curing but are often of little concern for EB curing, even for thick layers. The penetration "distance," in mg/cm^2, will differ only slightly from that of a clear lacquer. In an ink or paint containing finely divided, dense inorganic pigment, some of the electrons are "stopped" by the pigment. Such electrons can nevertheless induce chemical reactions in nearby regions of the organic matrix [21,22]. More difficulty is likely to be encountered not with inorganic pigments but with organic ones, which contain complex aromatic ring systems liable to change color on irradiation. In addition, aromatic ring molecules in solution often have a protective action, causing lower G-values for free radicals than would otherwise occur [22]. In many experiments, however, these potential difficulties with pigments have been realized only marginally or not at all [21,23].

IV ULTRAVIOLET CURING-PHOTOINITIATORS AND EQUIPMENT

A Photoinitiators

A very comprehensive list of photoinitiation systems, as of 1968, was given by Oster and Yang [24]. Only a few classes of these compounds seem to have been used in UV cured coating formulations although early patents cover many others, e.g. numerous halogen and sulfur compounds [25]. The agents most often used have been grouped systematically by several authors [25-27]. Although the classifications of many two-component initiators overlap, the following six groups are often distinguished:

Type 1: Initiators that generate radicals by direct photofragmentation. Especially prominent are the two subgroups based on the chemical structures given below:

a Benzoin ethers, which are cleaved as indicated in Figure 7. There is some evidence that the ether radical is less efficient than the benzoyl when radical concentrations are high and monomer concentrations low [28]. The storage stability of this compound tends to be inferior to some others.

b Substituted acetophenones; among these, 2,2-dimethoxy-2-phenylacetophenone undergoes Norrish Type I fragmentation, illustrated in Figure 8. The dimethoxy radical undergoes further fragmentation; Figure 9 gives an example. In contrast, chemically similar 2,2-diethoxyacetophenone undergoes the Norrish Type II decomposition outlined in Figure 10, in which the intermediate biradical can add directly to acrylate monomers. In the absence of monomer, the biradical isomerizes to a cyclic compound which undergoes the further decomposition shown in Figure 11.

Type 2: Systems that form radicals by bimolecular hydrogen transfer. An example is the photoexcited triplet state of diphenyl ketone, or benzophenone, which then undergoes the hydrogen transfer reaction indicated in Figure 12. Hydrogen abstraction also occurs in the primary step for the thiol-ene system. This will be described in more detail later but is outlined briefly below:

$$\text{[aromatic carbonyl compound]} \xrightarrow{h\nu} \text{[singlet excited state]} \longrightarrow$$

$$\text{[triplet excited state]} \xrightarrow{\text{R-S-H}}$$

$$\text{[reduced form of aromatic carbonyl compound]} + \text{R-S}\cdot$$

Type 3: Systems that form radicals by electron transfer or via a donor-acceptor complex, also known as an exciplex. The electron transfer

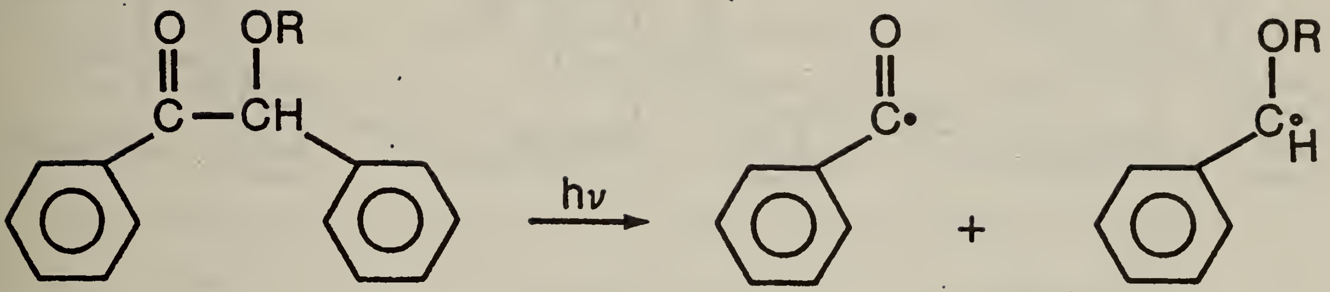


FIGURE 7 Type 1 photoinitiation with a benzoin ether.

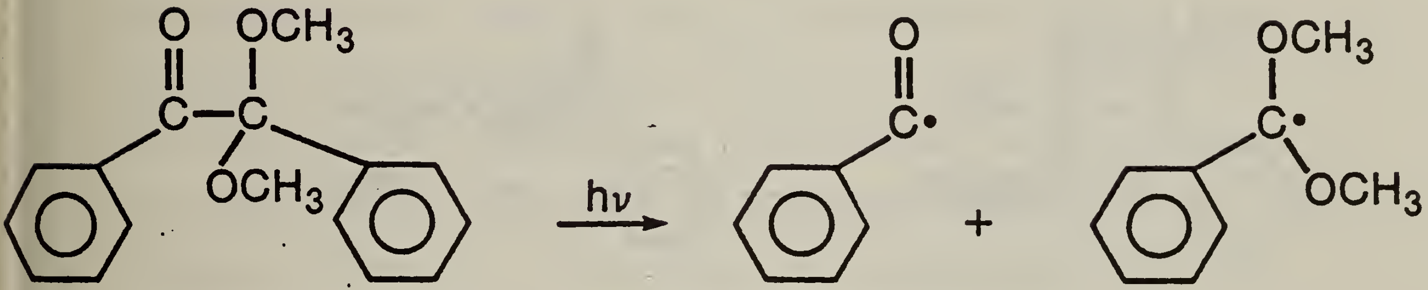


FIGURE 8 Norrish Type I fragmentation of the type 1 photoinitiator 2,2-dimethoxy-2-phenylacetophenone.

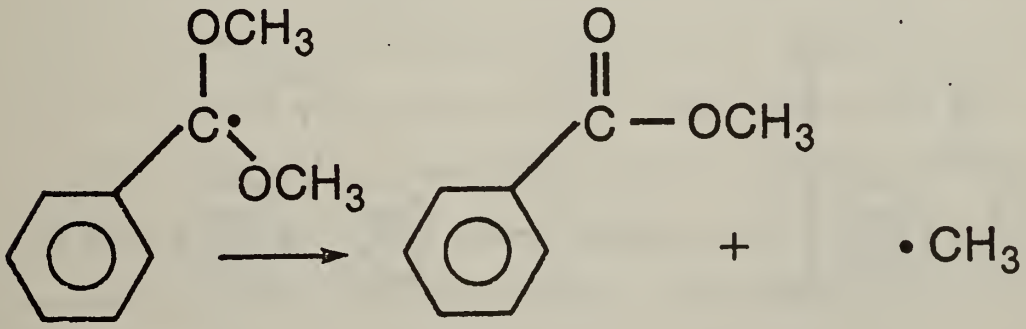


FIGURE 9 Further fragmentation of a product of the Norrish Type I reaction in Figure 8.

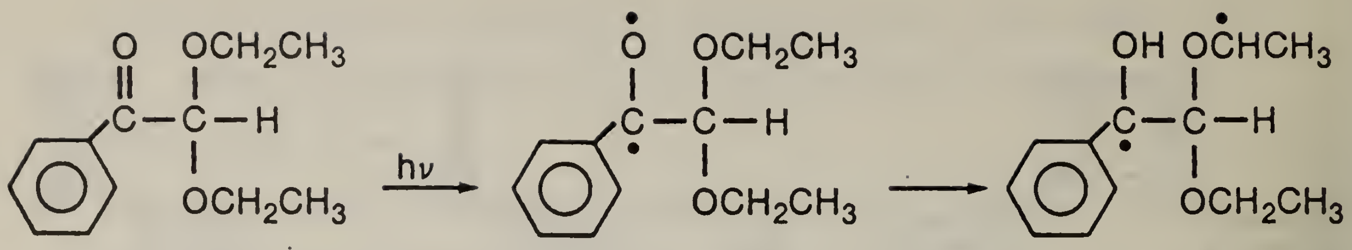


FIGURE 10 Norrish Type II decomposition of the type 1 photoinitiator 2,2-diethoxyacetophenone.

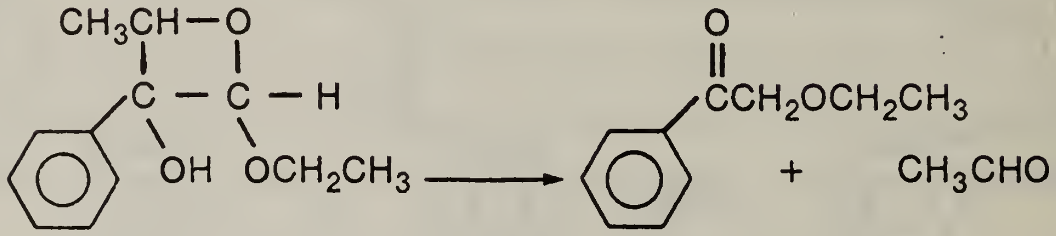


FIGURE 11 Decomposition of the coupling product formed from the biradical shown in Figure 10.

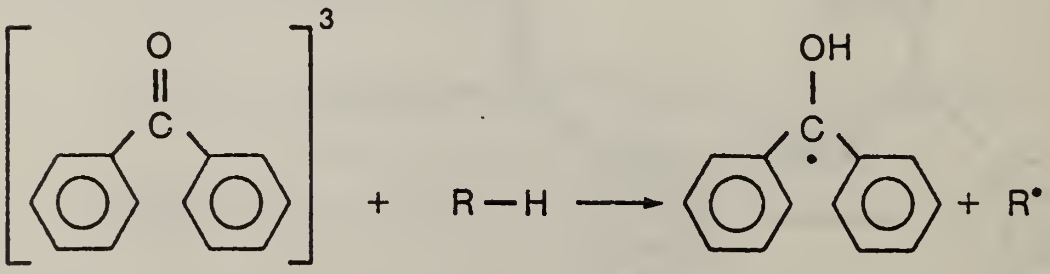


FIGURE 12 Type 2 photoinitiation with photoexcited diphenyl ketone.

is generally followed by proton transfer and the distinction from type 2 is not always clear. Figure 13 gives an example of this reaction with a tertiary amine acceptor, again for diphenyl ketone. A number of correlations have been made concerning the electron transfer initiation which occurs between the carbonyl and amine reactants,mainly involving the ionization potentials of the amines and the Taft polar and steric σ parameters used to quantitate relative reactivities of the carbonyls [25]. It is suggested that the amine radical is also especially reactive with oxygen, usually an inhibitor, in such a way as to generate further polymerization-initiating radicals [27] as illustrated in Figure 14. Methyldiethanolamine, $CH_3N(CH_2CH_2OH)_2$, is an especially effective amine component but many tertiary amines are active. Although there may be some doubt about the validity of the mechanism above, in practice amine-containing initiator combinations are often used in formulations for curing in the presence of air. An unfortunate consequence is the tendency of amine systems to generate yellow colored by-products.

Type 4: Photosensitizers that are used in combination with a radical-generating initiator. The sensitizer absorbs light energy and transfers it to the real initiator. An example of thioxanthone plus quinoline sulfonyl chloride [25] is outlined in Figure 15. Thioxanthone alone does not seem to initiate photopolymerization. Quinoline sulfonyl chloride can initiate with 310 to 330 nm UV light exposure but does not absorb at 370 to 380 nm. A combination of the two, however, initiates with 370 to 380 nm light. This method can be a useful feature for coatings containing titanium white pigments, which absorb at the lower wavelengths needed to initiate UV cures with quinoline sulfonyl chloride alone. In other combinations, the action of thioxanthone is much more conventional, like that of the ketones described under type 2 initiators.

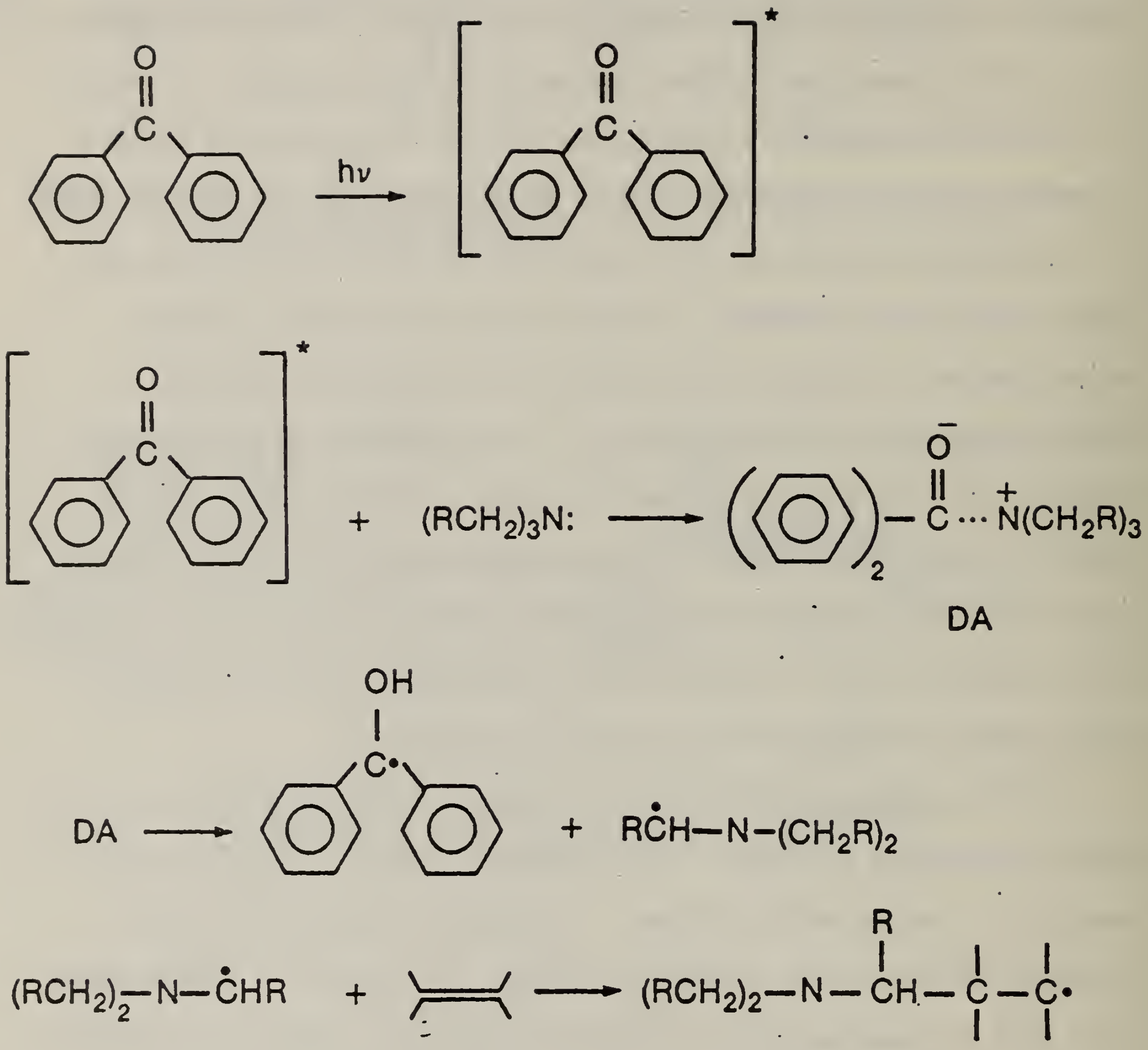
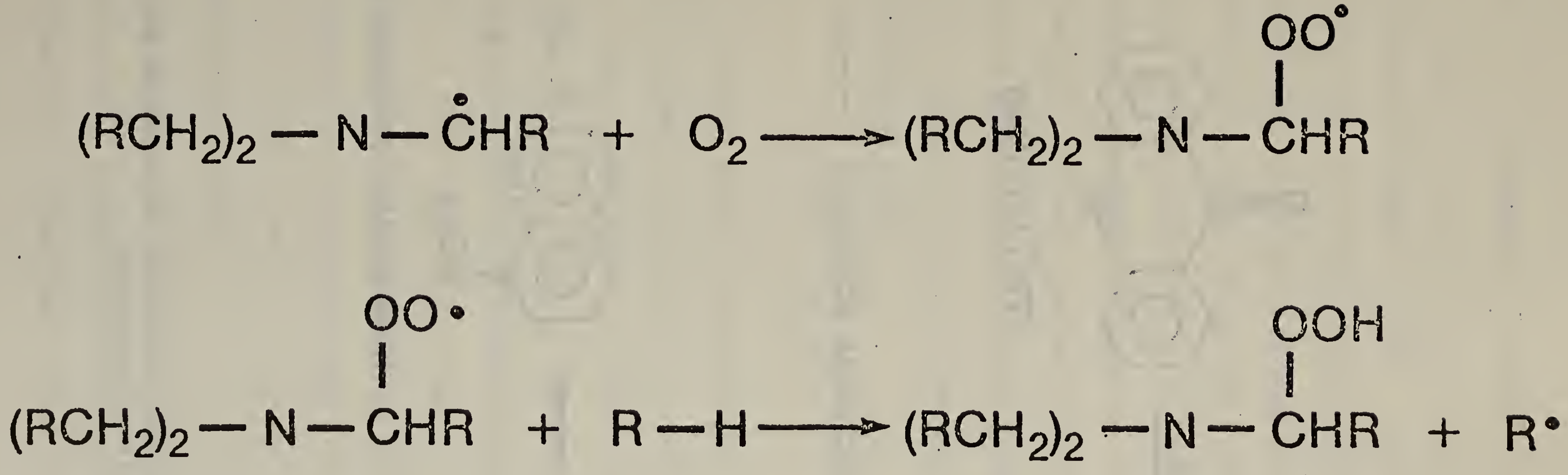


FIGURE 13 Type 3 photoinitiation with diphenyl ketone.



$$(RCH_2)_2-N-\dot{C}HR + O_2 \longrightarrow (RCH_2)_2-N-\overset{\overset{OO^\circ}{|}}{C}HR$$

$$(RCH_2)_2-N-\overset{\overset{OO\bullet}{|}}{C}HR + R-H \longrightarrow (RCH_2)_2-N-\overset{\overset{OOH}{|}}{C}HR + R\bullet$$

FIGURE 14 Generation of polymerization-initiating radicals by the reaction of oxygen with a type 3 photoinitiation reaction product from Figure 13.

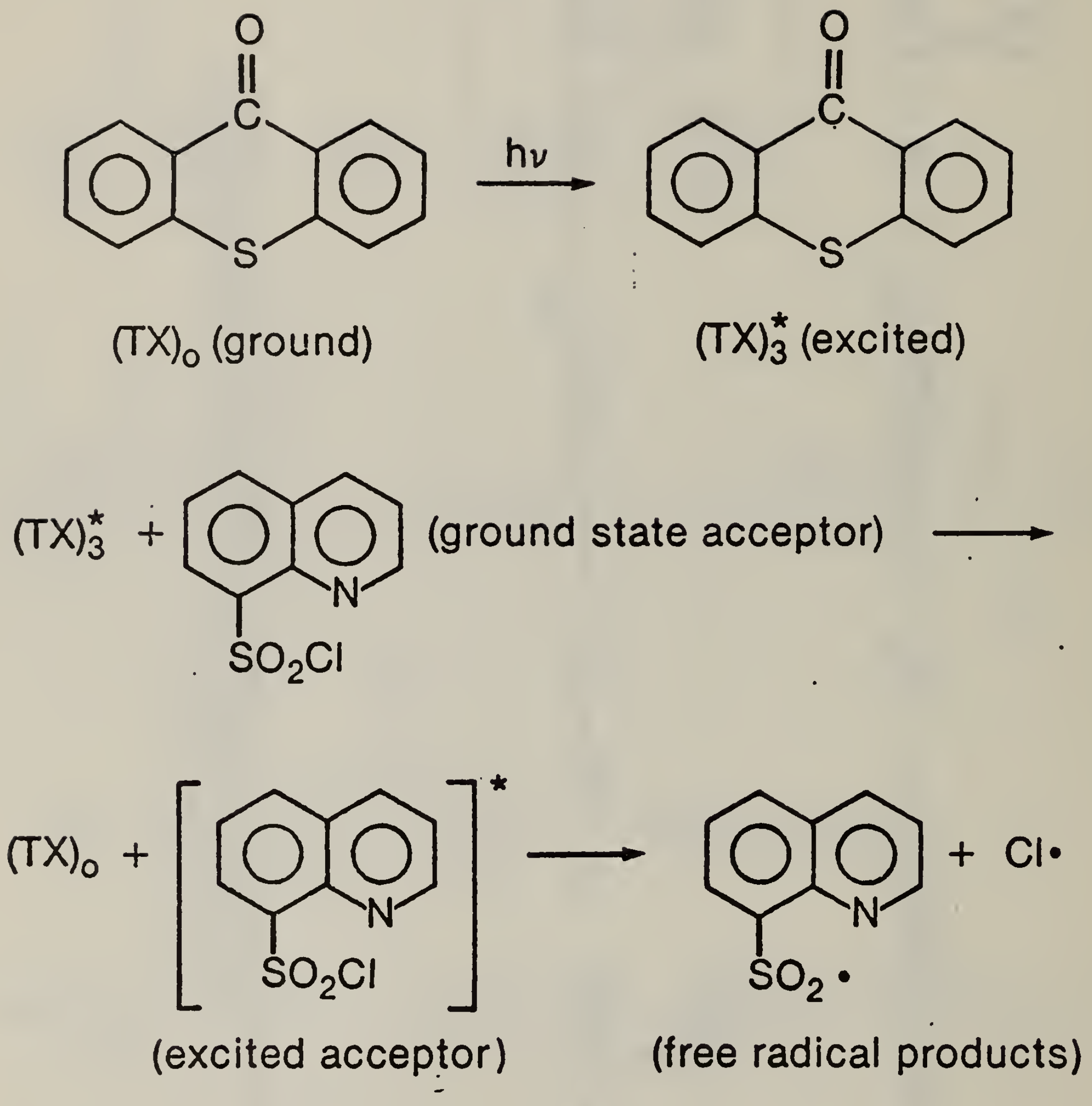


FIGURE 15 Type 4 photoinitiation with sensitizer thioxanthone and initiator quinoline sulfonyl chloride.

Type 5: This fundamentally different type is represented by the cationic initiators, which photolyze to strong Lewis acids that operate on epoxy-functional monomers [29-34]. The first commercial example, given in Figure 16, used aryldiazonium salts of complex halide anions. The Lewis acid (PF_5 in the above example) may initiate directly or react with water or alcohols to generate strong proton acids, as indicated in Figure 17. If the Lewis acid is the initiating species, the polymerization reaction is as shown in Figure 18. One of several disadvantages of diazonium salts is their liberation of nitrogen, which forms bubbles and pinholes in films over 15 µm thick; another is storage instability. These drawbacks were partially overcome by the use of diaryliodonium and triarylsulfonium salts:

$$Ar_2I^+X^-, \quad Ar_3S^+X^-$$

where X^- is a cation of low nucleophilicity, such as PF_6^-. There has been some development of more complex aryl groups to extend the absorption spectrum to longer wavelengths, and some use of added photosensitizers. At least four companies, including the American Can Company and the General Electric Company, hold patents in this area [35].

Type 6: A final individual instance of nonradical initiation occurs with amine salts of α-ketocarboxylic acids [36], for example the tributyl ammonium salt of phenylglyoxylic acid as indicated in Figure 19, which liberates the free amine to initiate the formation of polyurethanes from isocyanates and polyols.

Comparative tests of storage stability, cure speed, and numerous film properties of a standard formulation have been reported [37] for a number of commercial photoinitiators that produce free radicals in

$$\mathrm{Ar\,N_2^{+}\,PF_6^{-}} \xrightarrow{h\nu} \mathrm{Ar\,F + PF_5 + N_2}$$

FIGURE 16 Type 5 photoinitiation with an aryldiazonium salt.

$$\mathrm{PF_5 + ROH} \longrightarrow \mathrm{H^{+}\,PF_5\,(OR)^{-}}$$

FIGURE 17 Formation of a strong proton acid from addition of water or an alcohol to a product of the type 5 photoinitiation reaction in Figure 16.

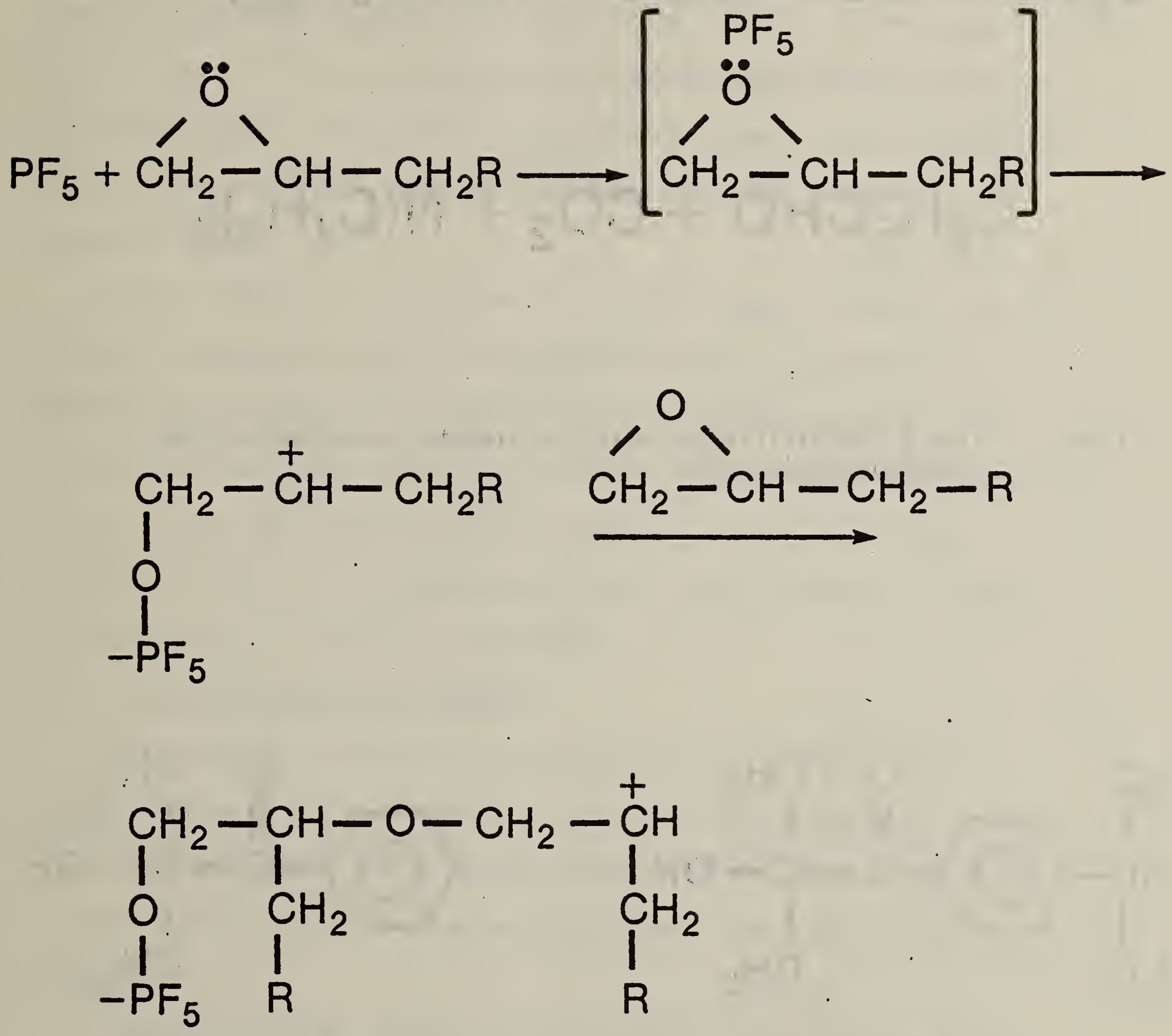
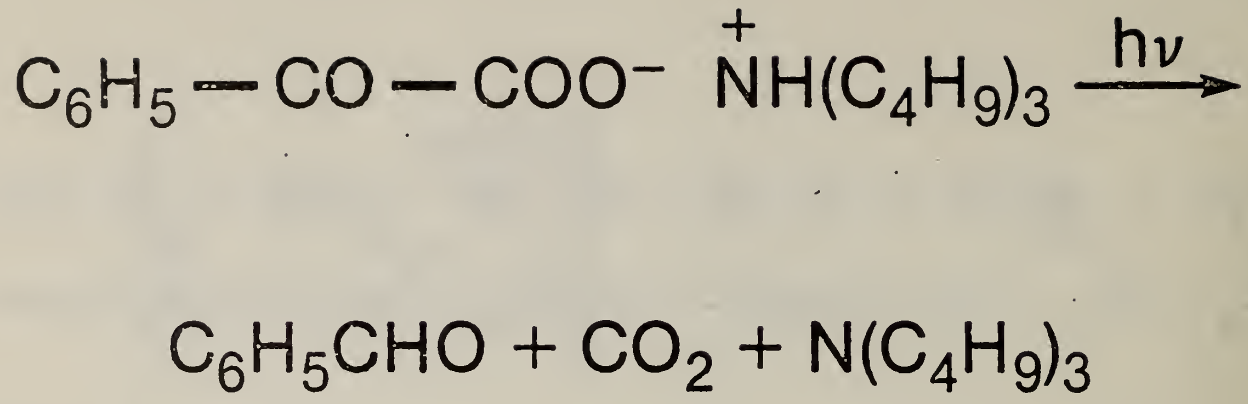
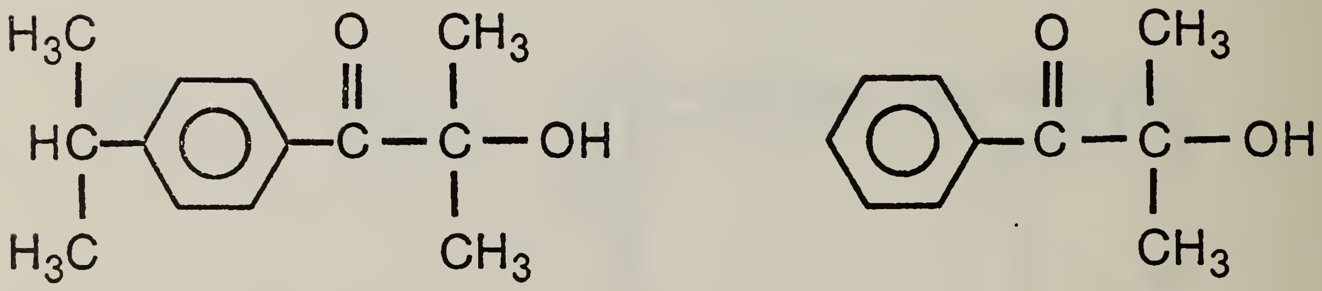


FIGURE 18 Polymerization reaction initiated by the Lewis acid product of the type 5 photoinitiation reaction in Figure 16.



$$C_6H_5-CO-COO^- \ \overset{+}{N}H(C_4H_9)_3 \xrightarrow{h\nu} C_6H_5CHO + CO_2 + N(C_4H_9)_3$$

FIGURE 19 Type 6 photoinitiation with the tributyl ammonium salt of phenylglyoxylic acid.



Merck Darocur 1116

Darocur 1173

FIGURE 20 Two commercial dialkylhydroxyacetophenone type photoinitiators.

acrylated resin mixtures. The chemical names, structural formulas, trade names, and important properties of these initiators are listed in Table 6. Among other recent disclosures are mixed alkyl (primarily dodecyl) thioxanthones [38], which are liquid, readily soluble, and initiate well in inks, and the two dialkylhydroxyacetophenones given in Figure 20 [39,40], which have a low yellowing tendency and low toxicity. At least one commercial cationic initiator, Uvcat-14, has been employed [34].

Often, mixtures of initiators of different types are used, for example, a benzophenone amine initiator for curing the surface and a dialkoxyacetophenone to cure the bulk of the formulation [41]. The mechanism of action may be obscure for many of these proprietary combinations. Pappas has proposed a kind of chemical synergism for some combinations [26]. The cooperative action of aryl ketones and amines is sometimes also labeled as synergistic.

B Lamps and Associated Equipment

The market for radiation curing of coatings is dominated by UV partly because of the development of high-intensity, relatively durable, and reliable medium-pressure mercury lamps. The following description of such lamps is based on Lacey and Keough [42], who give further details.

Clear fused quartz tubing is used to contain the plasma (mercury vapor of several atmospheres pressure at the operating temperature) that produces the ultraviolet light. The tubing normally has a wall thickness of 1 mm and an outer diameter of 20 to 25 mm. Lamp lengths may be one meter or more. The ends are sealed around the electrode ribbons to provide a vacuum tight enclosure. The electrodes are sophisticated electron emitters and current coupling devices, usually a rod

TABLE 6

Commercial Photoinitiators, Suppliers, and Selected Properties

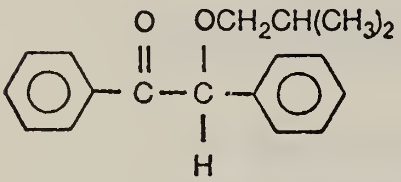
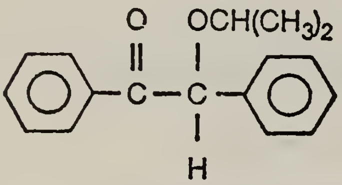
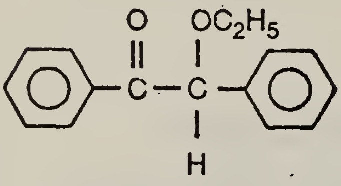
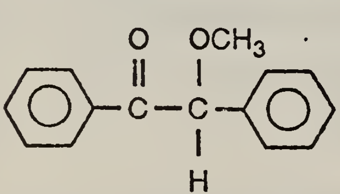
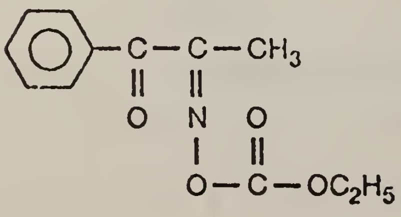
Generic Class/ Product Structure	Trade Name	Supplier	Physical State	Solubility	Optimum Absorption, nm
1 Benzoin Ether (type 1)					
Benzoin isobutyl ether 	Vicure 10	Stauffer Chemical	Liquid	Excellent	240-270
Benzoin isopropyl ether 	Vicure 30	Stauffer Chemical	Solid	Good	240-260
Benzoin ethyl ether 	None	Pfaltz and Bauer	Solid	Good	--
Benzoin methyl ether 	None	Pfaltz and Bauer	Solid	Good	300-380
2 Alpha-Acryloxime Ester (type 1)					
1-Phenyl-1,2-propanedione-2-(O-ethoxycarbonyl) oxime 	Quantacure PDO	Aceto Chemical	Solid	Good	275-400

TABLE 6 (continued)

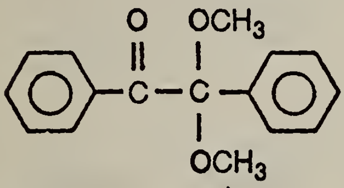
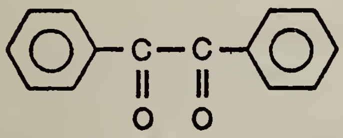
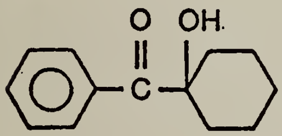
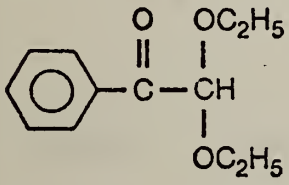
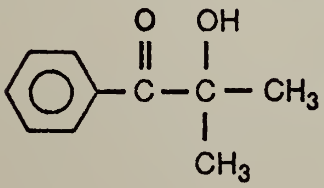
Generic Class/ Product Structure	Trade Name	Supplier	Physical State	Solubility	Optimum Absorption, nm
3 Benzil Ketal (type 1)					
2,2-Dimethoxy-2-phenyl-acetophenone 	Irgacure 651	Ciba-Geigy	Solid	Good	250-350
Benzil 	None	Pfaltz and Bauer	Solid	Good	320-450
Hydroxy cyclohexyl phenyl ketone 	Irgacure 184	Ciba-Geigy	Solid	Good	250-319
4 Acetophenone Derivative (type 1)					
Diethoxyacetophenone 	DEAP	Upjohn	Liquid	Excellent	240-350
2-Hydroxy-2-methyl-1 phenyl-propan-1-one 	Darocure 1173	EM Chemical	Liquid	Excellent	200-300

TABLE 6 (continued)

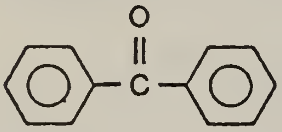
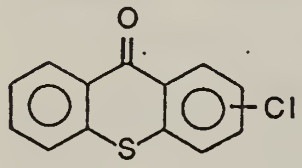
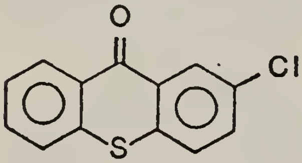
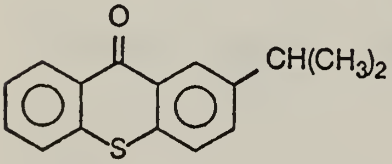
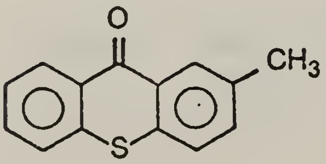
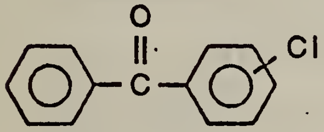
Generic Class/ Product Structure	Trade Name	Supplier	Physical State	Solubility	Optimum Absorption, nm
5 Ketone-(Ketone-amine) Combination (type 2,3)					
Benzophenone 	None	Upjohn	Solid	Good	240-350
Chlorothioxanthone 	Ultracure I-100	Sherwin-Williams	Solid	Fair	275-400
2-Chlorothioxanthone 	Quantacure CTX	Aceto Chemical	Solid	Fair	200-400
Isopropyl thioxanthone 	Quantacure ITX	Aceto Chemical	Solid	Good	250-400
2-Methylthioxanthone 	Quantacure MTX	Aceto Chemical	Solid	Fair	250-400

TABLE 6 (continued)

Generic Class/ Product Structure	Trade Name	Supplier	Physical State	Solubility	Optimum Absorption, nm
5 Ketone-(Ketone-amine) Combination (type 2,3) (continued)					
Chlorine Functional Substituted Benzophenone 	Acetocure X-500	Aceto Chemical	Solid	Good	--
Halogen Substituted Alkyl Aryl Ketone	Sandoray 1000	Sandoz	Solid	Good	240-360

Source: R. A. Lieberman, Radiat. Curing 8(3), 13 (1981).

of tungsten wrapped with a coil of tungsten wire, the whole covered with an electron emitting material such as barium oxide. Alternatively, the wire wrapping can encapsulate rare earth metals or other electron emitting materials. Molybdenum ribbon leads go out to the end caps. The quantity of mercury and amount and type of starting gas enclosed in the tube vary with the manufacturer but are designed to attain the desired pressure at the final operating temperature. If the environment does not change, the lamp is a constant voltage device with an operating current determined by the impedance in series with it. Oil filled capacitors with a reactive transformer are commonly used for this purpose. The plasma has an exceedingly high temperature; however, the fused quartz body must be kept below 800 °C to prevent rapid devitrification and also above 600 °C to maintain stable operation and the desired spectral character. The sealed ends must not be heated above 300 °C or the seal will deteriorate rapidly. Lamp cooling must therefore be rather carefully controlled. Such lamps are often sold with a 1000 hour warranty; however, a 4500 hour life expectancy has been reported recently [43].

Spectral output depends strongly on the operating pressure which, in turn, is governed by the fill of mercury. At pressures of a few thousandths of an atmosphere, most of the energy of the lamp is in the 253.7 nm line but the power is only 4 W/cm or less. At two atmospheres, characteristic of the medium pressure lamps most used, the spectrum has more and broader lines and an additional continuum background. An appreciable fraction of the light output is in the visible and infrared. Table 7 compares the energy distribution in various spectral lines for a low and a medium-pressure UV lamp [44], while the output spectra of four typical medium-pressure European lamps are shown in Figure 21 [45].

TABLE 7

Energy Distribution in Low- and Medium-Pressure Mercury Lamps

	Relative Energy	
Wavelength, nm	Low-Pressure Mercury Lamp[a]	Medium-Pressure Mercury Lamp[b]
1367.3	---	15.3
1128.7	---	12.6
1014.0	---	40.6
579.0-577.0	10.14	76.5
546.1	0.88	93.0
435.8	1.00	77.5
407.8-404.5	0.39	42.2
366.3-365.0	0.54	100.0
334.1	0.03	9.3
313.2-312.6	0.60	49.9
302.8-302.2	0.06	23.9
296.7	0.20	16.6
289.4	0.04	6.0
280.4	0.02	9.3
275.3	0.03	2.7
270.0	---	4.0
265.5-265.2	0.05	15.3
257.1	---	6.0
253.7	100.00	16.6[c]
248.2	0.01	8.6
240.0	---	7.3
238.0	---	8.6
236.0	---	6.0
232.0	---	8.0
222.4	---	14.0

[a] Canrad-Hanovia, Inc. Newark, NJ, SC-2537 lamp.
[b] Canrad-Hanovia Type A, 673A, 550 W lamp.
[c] Reversed radiation.

Source: J. G. Calvert, J. N. Pitts, "Photochemistry," Wiley, New York, 1965, p. 696.

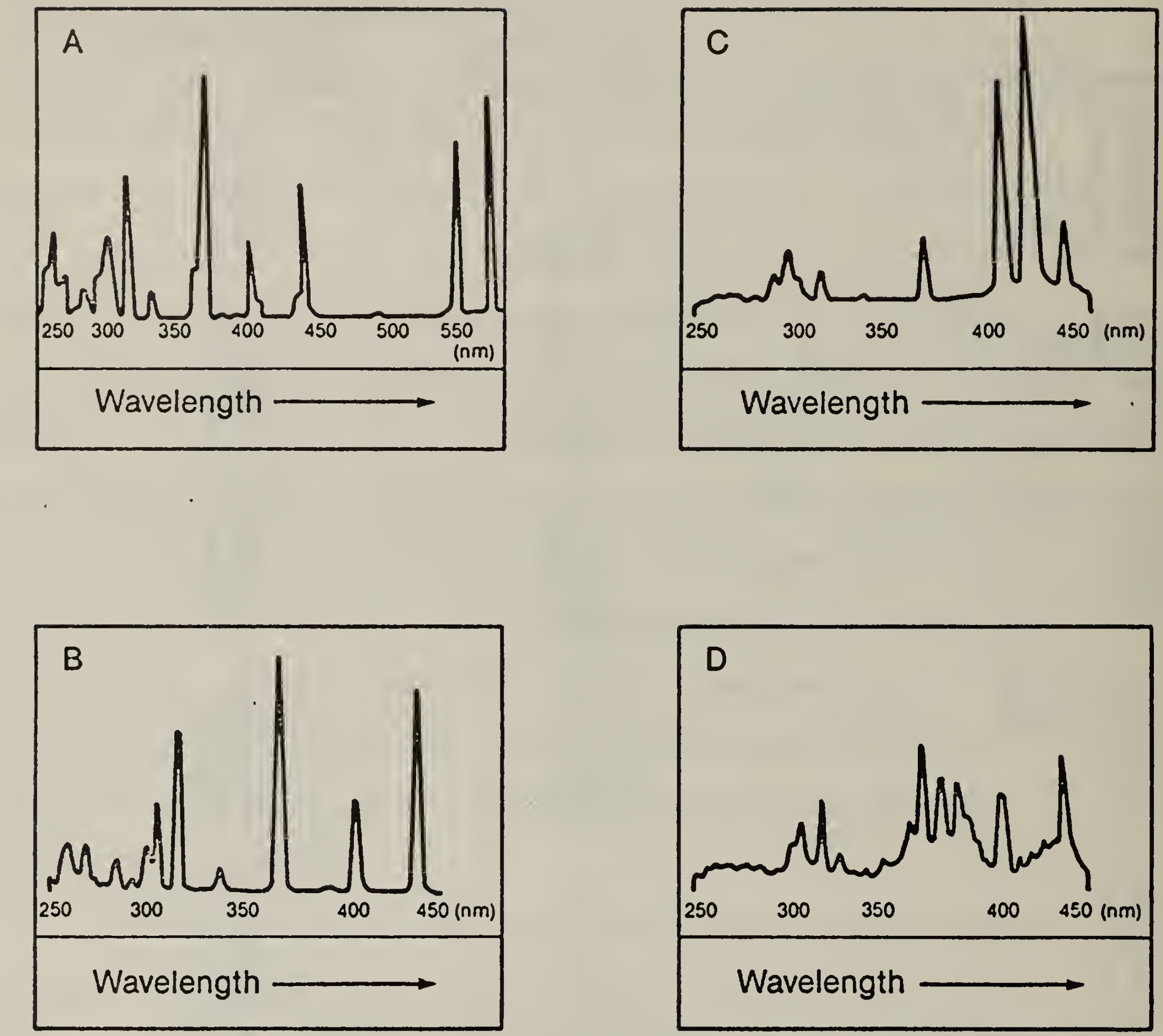


FIGURE 21 Output spectra of four European medium pressure mercury UV lamps: A, Philips HOK 80 W/cm; B, Theimer 5058 200 W/cm; C, Theimer 5050 200 W/cm; D, Theimer 5057 200 W/cm.

Further variation in UV output would be possible by doping with certain metals and halides, many of which are listed by McGinniss [46].

Pulsed xenon lamps have been employed to some extent; their output is generally richer in the visible part of the spectrum. Electrodeless medium pressure lamps, with the power fed in by microwaves, have been used also. The 254 nm low-pressure, so-called "germicidal," lamp has been incorporated into some combination systems. Most of these lamps require several minutes for start up and cannot be restarted too soon after shutdown without damage.

When installed in a production line, the lamps are mounted in irradiators which include lamp housings, cooling equipment, and reflectors that are usually elliptical and focus the light at the second focal point of the assembly. The material to be UV treated is typically carried under the lamps on a conveyor at about the focal distance of the reflector although the exact location is not always important [45,47]. To prevent damage in case of a conveyor stoppage, an automatically operated shutter or rotating reflector is needed to protect the work by blocking the intense light and heat exposure which would otherwise occur during a conveyor shutdown.

Ideally, it would be desirable if all the light emitted by the lamp were in a wavelength region absorbed by the photoinitiating system and utilized to generate free radicals or other active species. In practice, however, the most common initiators absorb in the region around and below 360 nm, and inspection of Figure 21 and Table 7 will show that much of the radiation of medium pressure lamps is outside this region. For this reason, the overall utilization of energy for initiation is less efficient in UV than for EB curing. The unusable radiation includes visible and considerable IR. Recently, filters have been developed to reject IR in cases where the temperature rise of the curing materials or substrate must be very carefully controlled [48]. It might be possible to use mixed UV and visible initiators to increase energy utilization. For instance, at least one initiator, camphorquinone, absorbs in the visible [26] and some dye sensitizers also operate in that range [24,25]. A few experiments have been reported on the visible light curing of polyesters using xenon lamps as the light source and a diketone with an amine as the two-part initiator [49].

C A Few Special UV Curing Problems

1 Initiator Concentration and Depth Variation of Cure

At a given wavelength, the initiator (in the absence of competing species) absorbs light according to the Lambert-Beer law:

$$\ln \frac{I(x)}{I(0)} = -\varepsilon c x$$

where I(x) is the light intensity remaining at depth x, I(0) is the incident light intensity, ε the extinction coefficient, and c the concentration of absorber. There has been much confusion over units and names for extinction coefficients and it is therefore advisable to examine the conventions used in a particular paper; for example, sometimes logarithms to the base ten are used in place of natural logarithms. According to this equation, if the extinction coefficient and concentration are both high, the light intensity will fall off very rapidly with increasing depth of penetration into the material. The surface layer will effectively screen the deeper layers against the penetration of UV light, resulting in undercure or even no cure in the lower layers. An optimum concentration of initiator therefore exists for a given layer thickness, below which the highest rate of cure cannot be attained and above which the overall rate of cure will decline. If a reasonably uniform cure is desired in all layers, sufficient light must reach the lowest layer. This in turn means that not all of the light intensity will be fully utilized. Mixtures of initiators absorbing with different ε values and/or light of a variety of wavelengths may sometimes alleviate this difficulty [50]. Pigments aggravate the light penetration problem by scattering or absorbing light, thus preventing it from traveling as far into the film as even the Lambert-Beer law would predict.

2 Pigments

At first sight, UV curing would appear to be incompatible with pigmented coatings. Nevertheless, with low enough pigment concentration or thin enough layers, UV curing has been widely successful with thin ink layers. Fillers such as silica and baryte, often used in lacquers, pose no great problems as they are sufficiently transparent to UV [51]. UV-visible absorption spectra of a number of frequently used organic pigments indicate small but definite transmission in the UV region [52,53]. This degree of UV transmission can be correlated with cure speed and depth.

As expected, carbon black has especially low transmission but 1 to 2 μm ink layers containing it can be cured successfully [47]. Various grades of carbon black differ somewhat in curing speed of the resulting ink formulation. A few experiments suggest that this is due not to radiation transmission differences alone but to the fact that some blacks contain surface carbonyl groups capable of terminating free radicals [54,55]. Titanium dioxide is a particular problem because, although transparent to visible light, it has a cut-off region at about 400 nm, below which it begins to absorb radiation with increasing efficiency. A few initiators, especially those containing substituted thioxanthones, are sufficiently active in the region around this cut-off and are especially useful in titanium white coatings. A small amount of titanium dioxide in a thin coating may actually give enhanced initiation. This phenomenon is usually attributed to the effects of refractive and reflective scattering, which give rise to an effectively longer lateral light path through the film [50,51] but a chemical contribution has also been suggested as an explanation by others [56].

3 Oxygen Inhibition

Oxygen generally acts to inhibit acrylate polymerizations. This is evident from the following mechanism. The reaction for addition of oxygen to a free radical:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

competes successfully with the addition of monomer:

$$R\cdot + M \rightarrow RM\cdot$$

Once the peroxy radicals form, the addition of monomer to these radicals:

$$RO_2\cdot + M \rightarrow ROOM\cdot$$

proceeds so slowly that the chain reaction is virtually stopped. The effect is especially pronounced at surfaces and in thin layers where the oxygen consumed is readily replaced by more diffusing in from the surrounding atmosphere.

The unfavorable effects of oxygen inhibition have been studied in detail [57] and are summarized as follows. When a mixture of acrylic urethane oligomer, 2-ethylhexyl acrylate, and 2,2-dimethylpropane-1,3-

diacrylate (neopentyl glycol diacrylate) with 2,2-dimethoxy-2-phenylacetophenone initiator and a very small amount of inhibitor was used, polymerization was immediate in pure nitrogen but in oxygen containing atmospheres showed an induction time period. The induction period increased in duration with decreasing ultraviolet intensity in such a way that a plot of induction period versus reciprocal intensity is linear. The slopes of such plots were greater with higher oxygen concentration. The overall rates of polymerization decreased as oxygen concentration increased, and in some cases the polymerization stopped short of completion. This occurred because the oxygen supplied continuously through diffusion eventually allowed peroxy radicals to form in preference to further polymerization, the rate of which was reduced by partial monomer consumption as the polymerization progressed. Polymerization could subsequently be carried to completion by converting to a nitrogen atmosphere. In oxygen, the degree of polymerization and kinetic chain lengths were lowered, as expected. These two results--incomplete polymerization and lower relative molecular mass--account for the tacky surface layer often found when deeper layers of a coating have hardened satisfactorily.

Oxygen inhibition can interfere with both UV and EB curing mechanisms. It is usually not important in EB curing of coatings since inert atmospheres are necessary in EB in order to reduce the relatively large amounts of ozone which would otherwise be produced in air. In UV curing, less drastic measures than an inert atmosphere are normally adequate to reduce ozone levels. Thus, oxygen is usually present and contributes to the inhibition of curing. One factor unique to UV curing is the air flow needed to cool the lamps, which tends to sweep away ozone but draw in more oxygen [58].

Among early methods suggested to reduce oxygen inhibition was a two-stage cure. A low pressure 254 nm lamp in an inert atmosphere produces a thin surface cure because of the very high absorption coefficient of most initiators at 254 nm. This surface polymer skin then retards further diffusion of new oxygen into the mixture and allows a cure in depth to follow in a normal air atmosphere with medium pressure lamps radiating mostly longer UV wavelengths. A xenon flash lamp stage could be substituted for the 254 nm lamp. Its high intensity consumes oxygen by converting it to peroxy radicals in the bulk film at a rate much faster than the oxygen can be replaced by diffusion in from the air [59]. A more sophisticated procedure has also been proposed in which red light and a dye sensitizer convert oxygen into singlet oxygen which, in turn, is scavenged by 1,3-diphenylisobenzofuran. The oxidation product can now serve as a main or auxiliary initiator when activated by UV light [60,61].

Recently there has been a trend favoring formulations which will cure satisfactorily in air. Those containing benzophenone plus methyldiethanolamine or other tertiary amines will often give satisfactory performance, especially when exposed to high ultraviolet light intensities [26,41,62]. The cationic initiators and reaction systems are insensitive to oxygen inhibition [31].

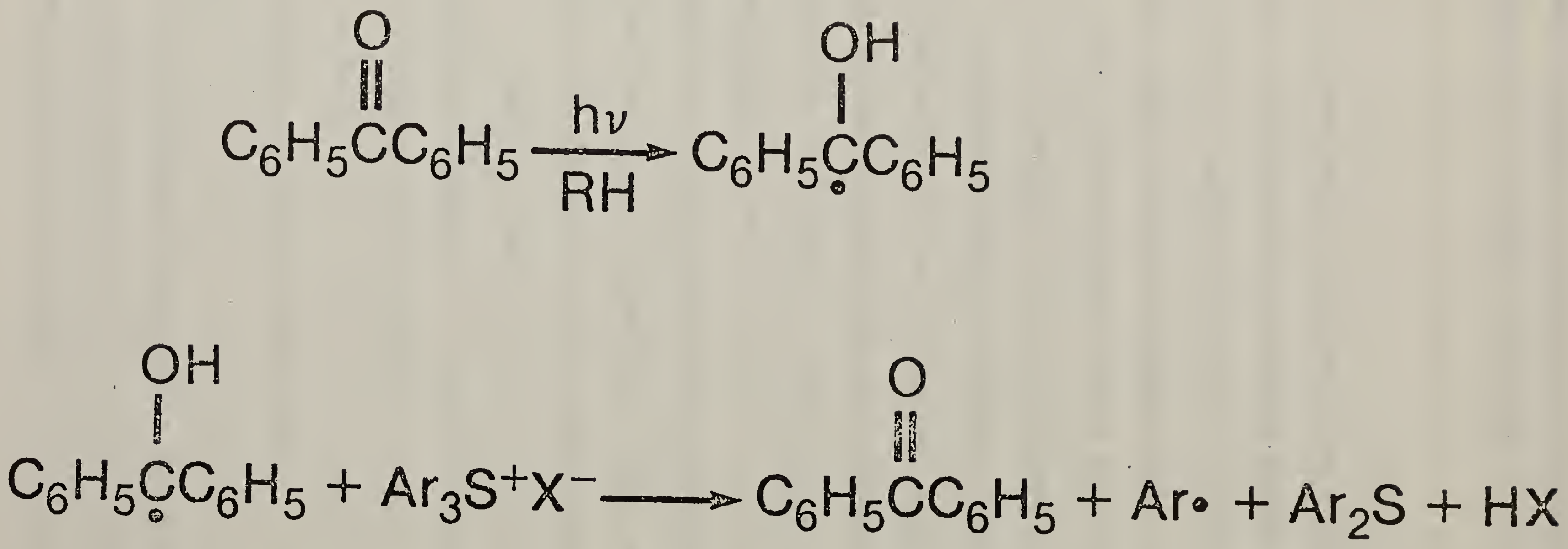
V UV AND EB RESIN SYSTEMS

A Oligomers

Most of the radiation curable coating systems are based on molecules containing acrylate functional groups and are crosslinkable by both UV and EB; however, three other systems are also commonly used: cationic, thiol-ene, and unsaturated polyester plus styrene or acrylate monomer. Representative oligomers for all of these resin systems are described below.

1 Cationic Systems

Cationic photoinitiators were described in the previous section on UV curing. Active cation species are difficult to produce reliably by EB irradiation so the use of cationic systems is restricted to UV formulations in practice. The oligomers are epoxy resins, such as would be used in other well-known kinds of epoxy coatings, and polymerize and crosslink by opening of the epoxide ring and not by free radical addition. Recently, hybrid systems have been described in which the polymerization is partly free radical and partly cationic [34]. Their formulation is more specialized, and typically includes an epoxy oligomer, a multifunctional acrylic monomer, a cationic photoinitiator, and benzophenone. Curing speeds and properties of the resulting coating are said to be a useful compromise between those of acrylic and epoxy types. Among other properties, adhesion to many metals is improved. Benzophenone appeared to accelerate the action of one cationic initiator by almost a factor of two even in the absence of acrylic monomer, whereas benzoin methyl ether was ineffective. The proposed mechanism of the accelerating effect involves the steps outlined in Figure 22. At most UV wavelengths, the benzophenone is a much better absorber than the primary cationic initiator. A disadvantage of cationic systems is the possible corrosion of metallic substrates by the Lewis acid liberated on initiation. This disadvantage is shared by the more conventional nonradiation cured epoxy coatings as well. An outstanding advantage of cationic systems is the ability of the initiator, once liberated, to



$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \xrightarrow[RH]{h\nu} C_6H_5\overset{\overset{\displaystyle OH}{|}}{\underset{\bullet}{C}}C_6H_5$$

$$C_6H_5\overset{\overset{\displaystyle OH}{|}}{\underset{\bullet}{C}}C_6H_5 + Ar_3S^+X^- \longrightarrow C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 + Ar\bullet + Ar_2S + HX$$

FIGURE 22 Mechanism for benzophenone acceleration of cationic initiation.

continue its activity a relatively long time after being removed from the UV source and, in pigmented coatings, to diffuse into deeper layers where irradiation might be ineffective and cause initiation there. Electron beams and other ionizing radiation can bring about cationic polymerization, but the specialized requirements, extreme dryness for example, are unlikely to be satisfied in coating formulations.

2. Thiol-ene Systems

The model reaction of the thiol-ene system [63] is the free radical addition of a thiol to an olefin, as illustrated in Figure 23. This reaction can occur upon irradiation by either an EB or UV source. If brought about by a photoexcited ketone, the alternative mechanism shown in Figure 24 is likely [64]. A linear chain polymer results if both the olefin and the thiol are bifunctional. A crosslinked network can be produced if one reactant is more than bifunctional, as is usually the case. For example, the reaction of a bifunctional polyene and a tetrafunctional polythiol is drawn schematically in Figure 25. The polyenes and polythiols are usually short polymer chains, below about 1000 g/mol, but some are "prepolymers" of relative molecular mass 1000 to 10,000 g/mol. Examples of commonly used thiols are: pentaerythritol tetrakis(thioglycolate), shown in Figure 26, and trimethylolethane tris(β-mercaptopropionate), Figure 27. The polyene component can be a complicated polymer type end-capped by double bond-containing moieties; see Figure 28 for an example. Changing the molecular structure of the diene "interior" can afford the great range of cured resin properties indicated in Table 8.

Thiol-ene systems were originally developed by W. R. Grace and Company for the preparation of photopolymer relief printing plates

$$RSH + CH_2{=}CHR' \xrightarrow{X\bullet} RSCH_2CH_2R'$$

FIGURE 23 Free radical addition of a thiol to an olefin in thiol-ene systems.

$$R_2C{=}O\ {}^3(n,\pi^*) + R'SH \longrightarrow R_2\overset{\bullet}{C}OH + R'S\bullet$$

$$2R_2\overset{\bullet}{C}OH \longrightarrow R_2C(OH)C(OH)R_2$$

$$R'S\bullet + CH_2{=}CHCH_2R'' \rightleftharpoons R'SCH_2\overset{\bullet}{C}HCH_2R''$$

$$R'SCH_2\overset{\bullet}{C}HCH_2R'' + R'SH \longrightarrow R'SCH_2CH_2CH_2R'' + R'S\bullet$$

FIGURE 24 Mechanism for the free radical addition of a thiol to an olefin in the presence of a photoexcited ketone.

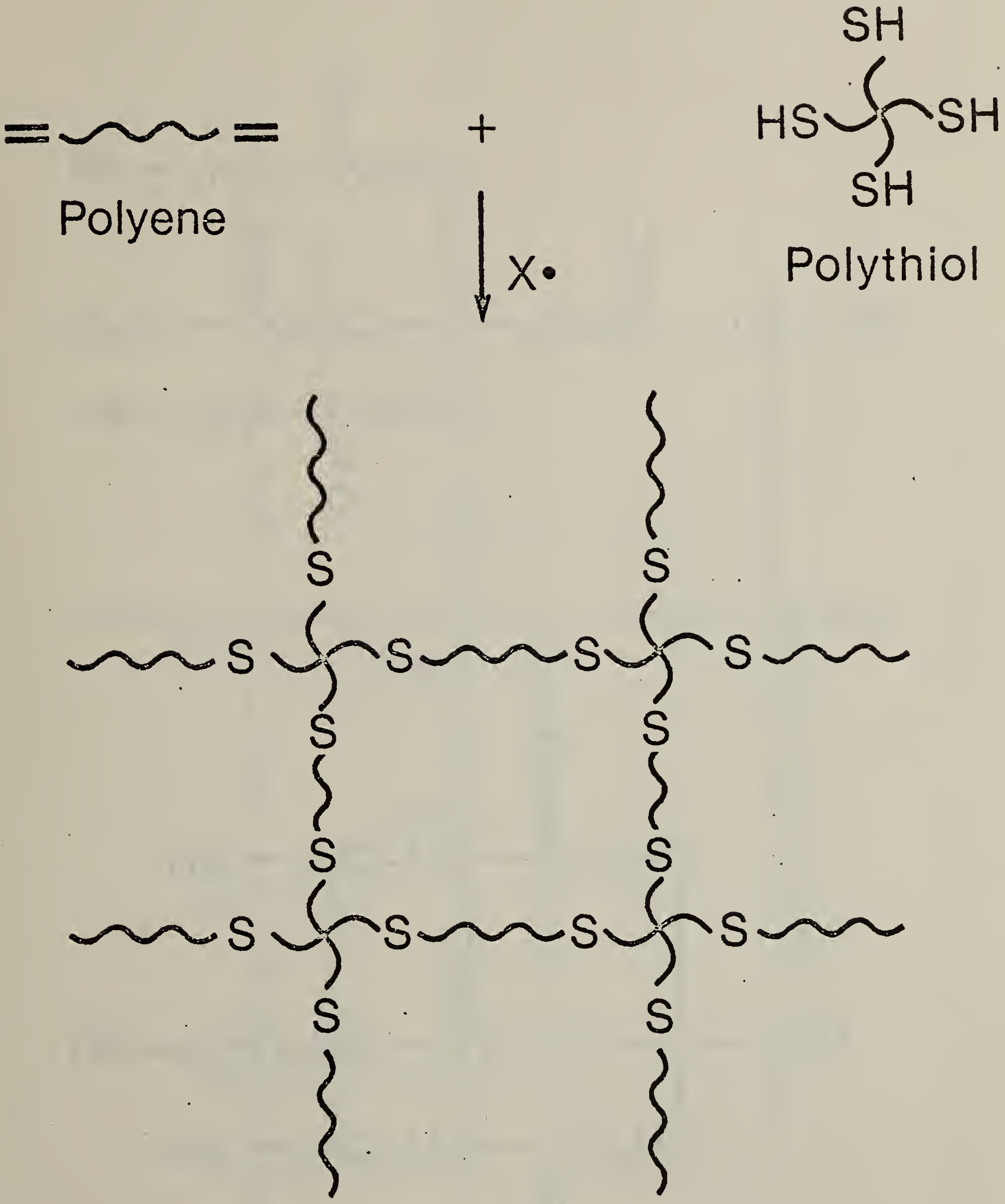


FIGURE 25 Formation of a crosslinked network from the thiol-ene reaction of a bifunctional polyene and a tetrafunctional polythiol.

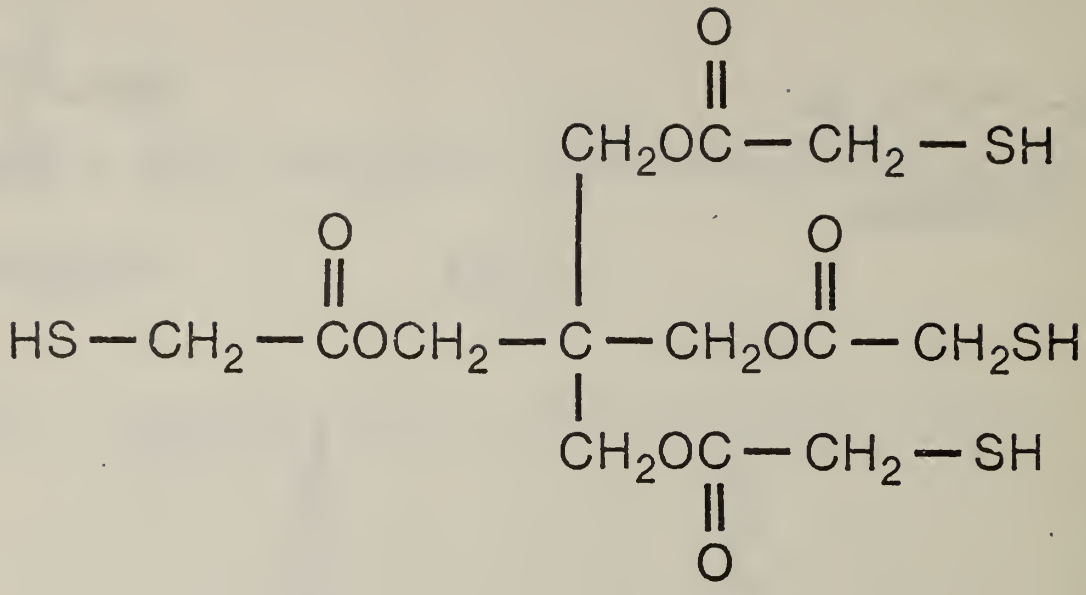


FIGURE 26 The tetrathiol pentaerythritol tetrakis(thioglycolate).

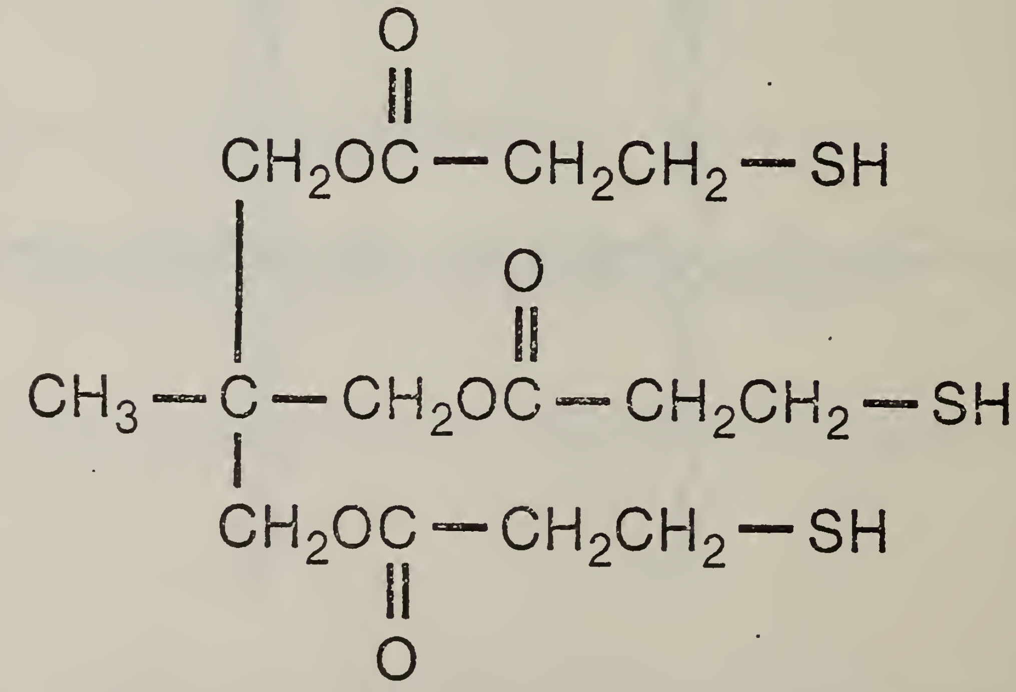
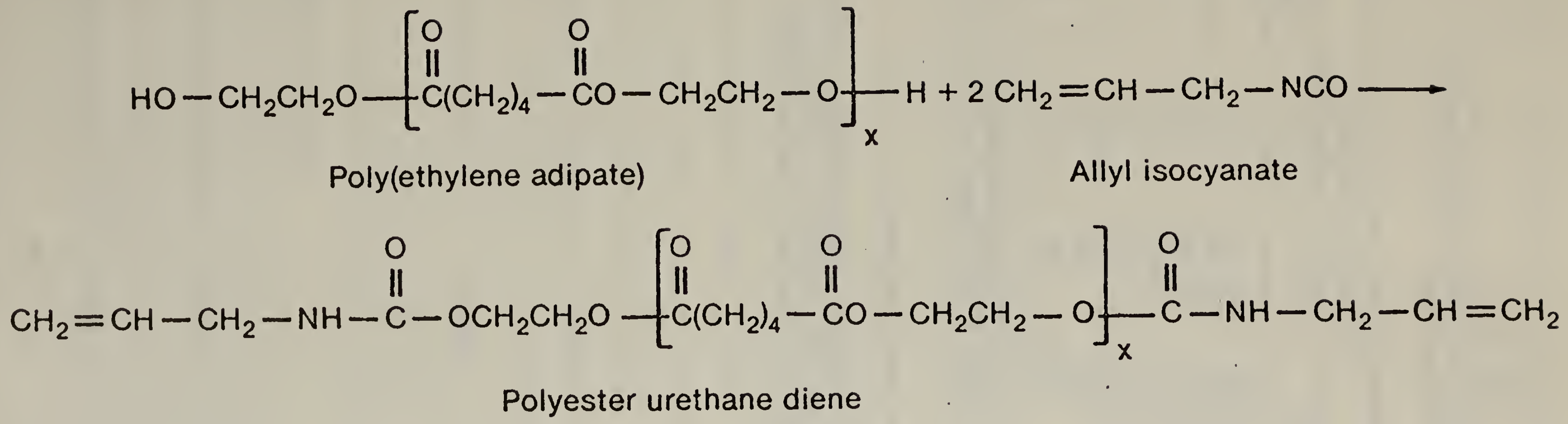


FIGURE 27 The trithiol trimethylolethane tris(β-mercaptopropionate).



$$HO-CH_2CH_2O-\left[\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}O-CH_2CH_2-O\right]_x-H + 2\,CH_2{=}CH-CH_2-NCO \longrightarrow$$

$$CH_2{=}CH-CH_2-NH-\overset{O}{\overset{\|}{C}}-OCH_2CH_2O-\left[\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}O-CH_2CH_2-O\right]_x-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH{=}CH_2$$

FIGURE 28 A polydiene oligomer formed by endcapping poly(ethylene adipate) with allyl isocyanate.

TABLE 8

Effect of Polyene Structure on Mechanical Properties of Thiol-ene Resins

	Mechanical Properties			
Polyene Structure[a]	Modulus, kPa	Tensile, kPa	Elongation, %	Hardness, Shore A
1 Melamine/3 TDI/3 AA	1,340,000	55,000	5	91
1 TDI/2 AA	841,000	18,100	90	89
1 EPON 828/2 DAA	152,000	15,900	78	76
1 TDI/2 DAA	133,000	6,620	70	90
1,2,4-Trivinylcyclohexane	15,400	2,070	15	70
Diallyl phthalate	5,240	965	30	70
1,5-Hexadiene	965	69	10	60
Tetraallyl orthosilicate	550	28	6	60

[a] EPON 828 = liquid epoxy resin product of Shell Chemical Co.
TDI = toluene diisocyanate (80/20 mixed isomers of 2,4- and 2,6-)
AA = allyl alcohol
DAA = diallyl amine
All UV cured with a tetrathiol and benzophenone.

Source: R. W. Bush, "Thiol-ene Radiation Curable Polymers and Practical Applications," Talk at Coatings Symposium, North Dakota State University, June 4, 1974; Text from W. R. Grace and Co.

used, for example, in the printing of newspapers [65], but are also suited for printing inks, wire coatings [66], and solder resists for the electronics industry [67]. Cheaper hybrid systems have been developed and might typically contain ten percent polythiol and forty percent diethylene glycol diacrylate with the balance of the resin an acrylated urethane oligomer. Suggested uses are overprint varnishes for cartons and book jackets and floor tile surface coatings [65]. One potential objection to the thiol-ene systems has been their odor during application, although it later disappears upon curing [68,69]. Air has hardly any effect on the curing speed of these systems.

3 Unsaturated Polyesters with Styrene or Acrylates

The unsaturated polyester-styrene combinations were among the earliest used in the radiation curing field. The polymer is a glycol-phthalic anhydride copolymer which contains maleic moieties in place of some of the phthalic groups to act as reactive sites for crosslinking. These compositions have been used in Europe, especially as finishes for wood products, where slower production speeds are tolerated [70]. These relatively slow curing systems contain highly volatile styrene or acrylate monomers. Evaporation of monomer is effectively retarded by incorporating a waxy hydrocarbon of critically-chosen molecular length into the formulation [71]. This strategy is unsuccessful for producing more useful resins with higher curing speeds, since there is no time for the wax to migrate to the surface layer where it exerts its influence.

4 Acrylate Systems

The much greater curing speed of systems containing acrylic monomers and acrylate-bearing oligomers has given these formulations the major share of the radiation cured coatings market. An early but detailed description of acrylate components is given by Vrancken [72].

He lists these five alternative ways of classifying the formulations:

a By the chemical class of the polymer backbone of the acrylated resin:

- polyester
- acrylic
- epoxy
- polyurethane
- polyether
- silicone

b By the nature of the unsaturated bond fixed on the polymer:

- acrylic, methacrylic, acrylamide
- "vinyl ester" (really linear polyethers esterified at the ends with acrylic acid)
- maleic, fumaric, itaconic, crotonic, etc.
- allylic
- styrenic
- vinyl ether
- olefinic
- acetylenic

c By the nature of the unsaturation in the monomer/solvent (as above)

d By the position of the unsaturation in the polymer:

- main chain
- pendant
- end group

e By the length of the polymer chain, relative molecular mass, or functionality, for example:

- polymers
- oligomers
- monomers

or:

- monounsaturated
- diunsaturated
- polyunsaturated

Not all the classes have received much interest in later years and only those selected for development will be mentioned here.

A typical acrylated resin is derived by endcapping bisphenol A diglycidyl ether with acrylic acid. This structure, ethoxylated bisphenol A dimethacrylate, is commonly called acrylated epoxy or sometimes, illogically, vinyl ester. Other chemical structures which could also be considered as acrylated epoxies are acrylic esters and fatty acid modified esters derived from epoxidized novolacs [73]. Recent summaries of important types [74] include these acrylated epoxies, illustrated in Figure 29, and also the acrylated urethanes and polyesters of Figure 30, and acrylated acrylics, commonly prepared as indicated in Figure 31. The acrylated epoxies can be hard and chemically resistant if derived from bisphenol A or soft and rubbery if derived from a long chain aliphatic diglycidyl ether. Acrylated urethanes give an optimum in flexibility and mar resistance but are expensive. Acrylated polyesters typically have film properties intermediate between those of the epoxy and urethane types. The acrylated acrylics perform well in exterior applications.

A special line of urethane acrylic oligomers with several different degrees of polymerization (Uvimer) are offered by the Polychrome Corporation. They are insensitive to oxygen and have good shelf life [62]. The oxygen insensitivity is believed to be due to the particular placement and type of unsaturation. Their structural formulas are given in Figure 32. The N-vinyl urethanes, which are <u>not</u> acrylated, seem to offer an unusual combination of reactivity with flexibility of the final product [75].

To the classes discussed above can be added the unsaturated aminoplasts [75], made by reacting urea-formaldehyde or melamine-formaldehyde prepolymers with 3-hydroxypropyl acrylate or other acrylates containing terminal hydroxy groups.

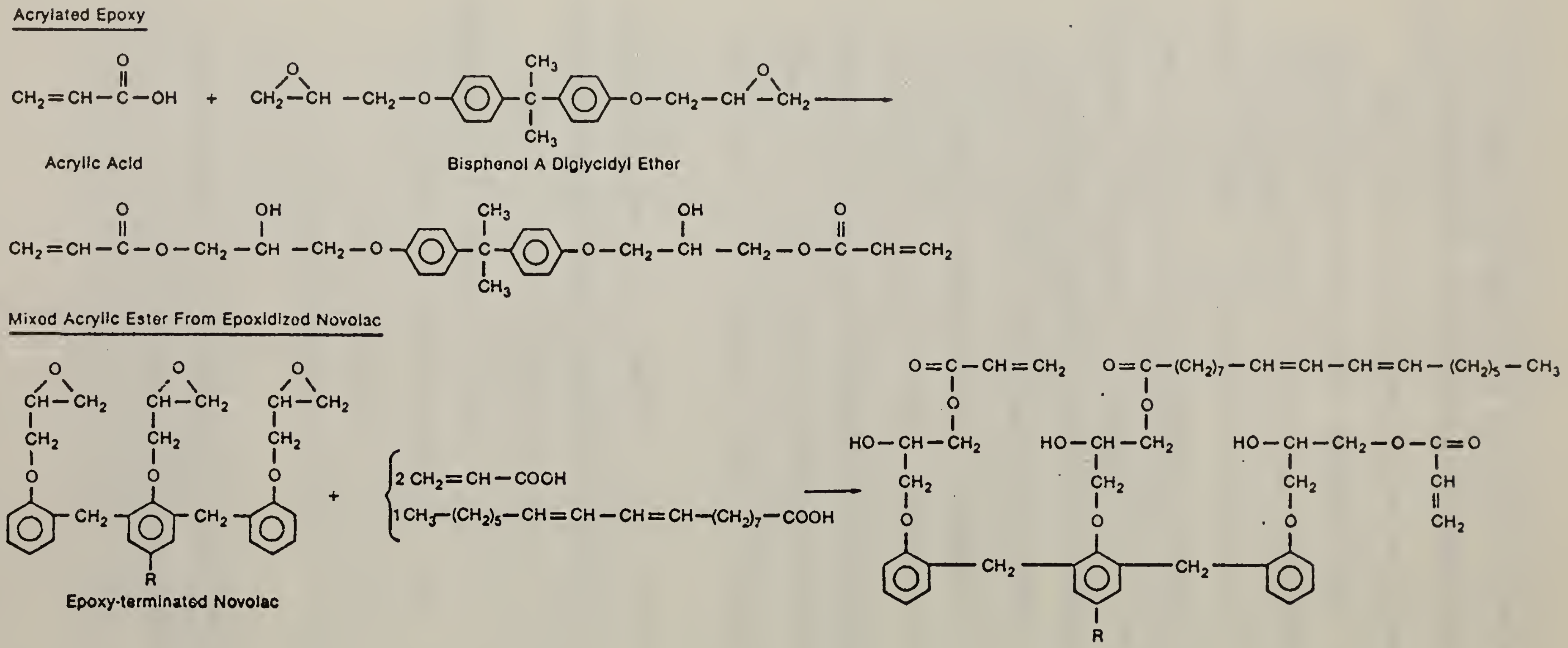


FIGURE 29 Acrylated epoxy oligomers derived from bisphenol A diglycidyl ether and epoxidized novolac.

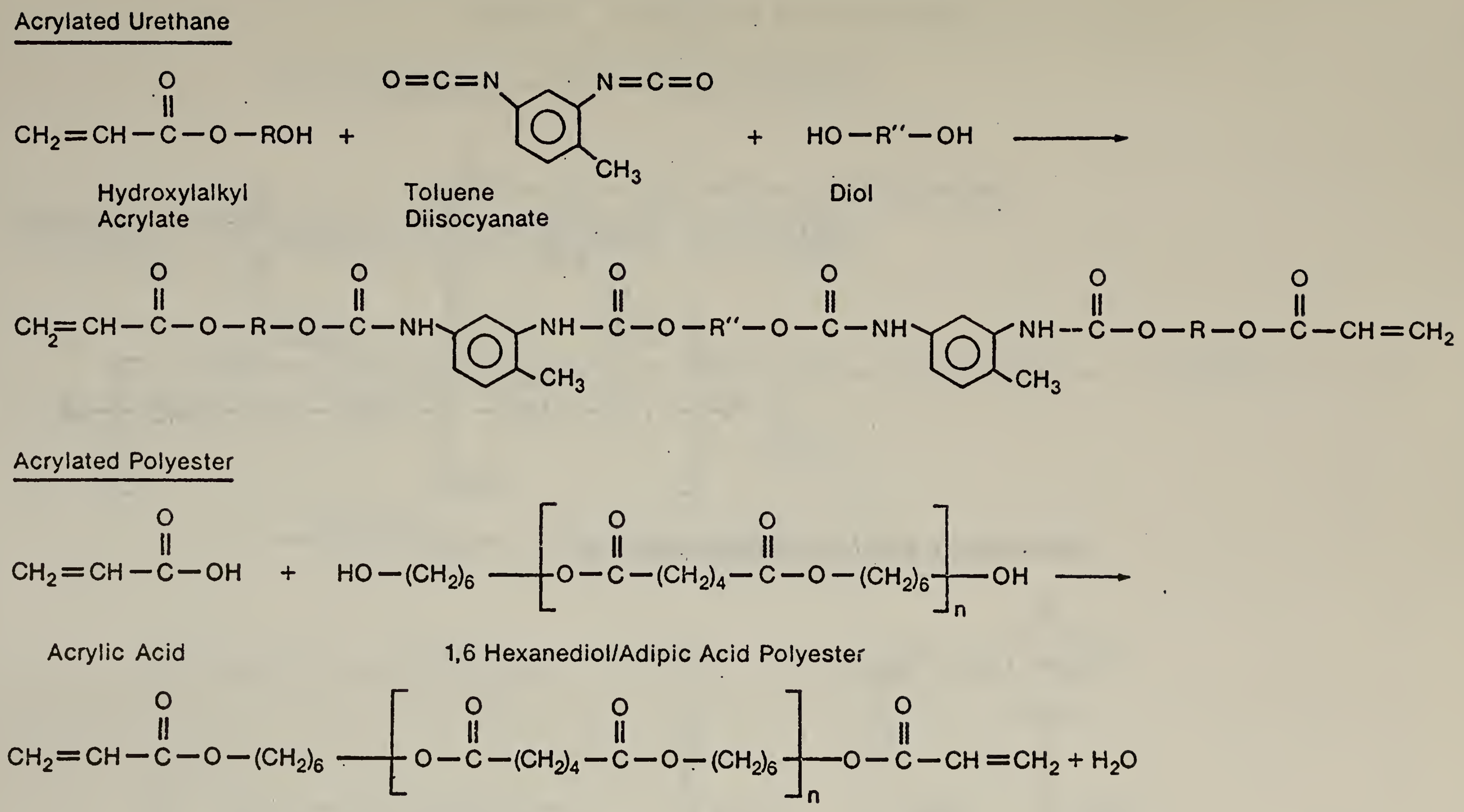


FIGURE 30 Acrylated urethane and polyester oligomers.

Acrylated Acrylic

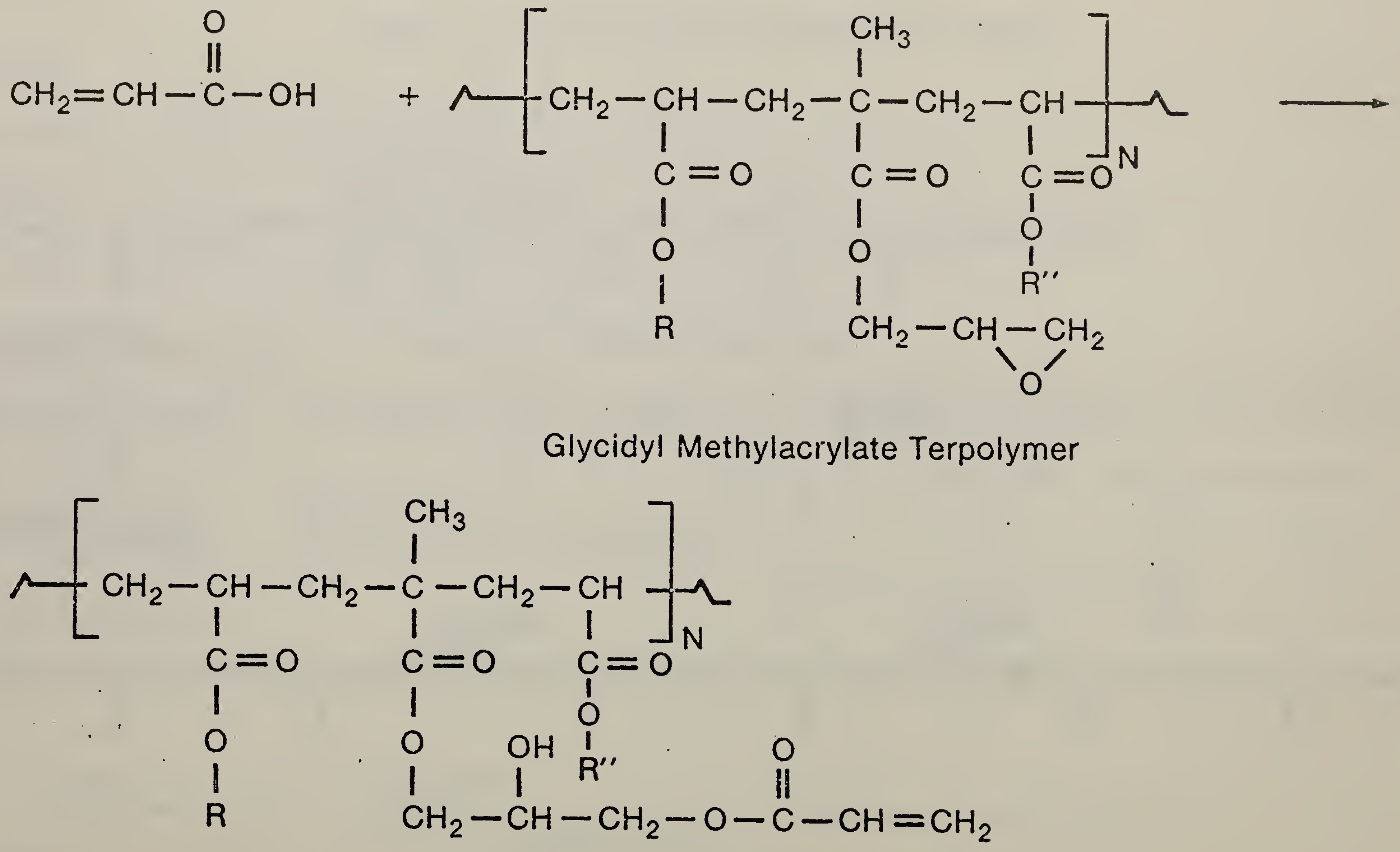
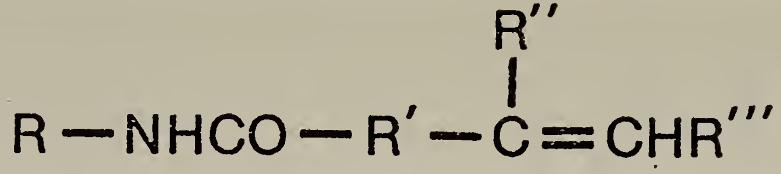
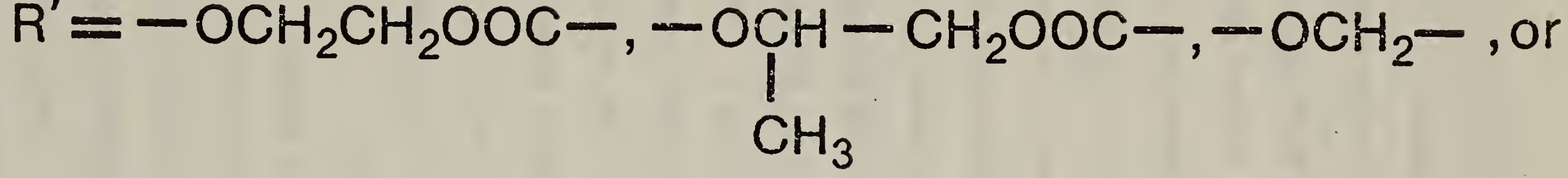


FIGURE 31 An acrylated acrylic oligomer.



$$R-NHCO-R'-\overset{\overset{\displaystyle R''}{|}}{C}=CHR'''$$

Where R ≡ Oligomer backbone structure



$$R' \equiv -OCH_2CH_2OOC-, -\underset{\underset{\displaystyle CH_3}{|}}{OCH}-CH_2OOC-, -OCH_2-, \text{or}$$

$-NHCH_2-$, for example

$R'' \equiv H-$ or CH_3-

$R''' \equiv H-$ or C_6H_5-

FIGURE 32 Chemical formulas of Uvimer acrylic urethane oligomers.

B Monomers or Reactive Diluents

A large number of mono-, di-, and polyfunctional acrylic monomers are now offered commercially. They are needed as diluents to reduce the viscosity of the formulated mixtures and to promote rapid curing. The polyfunctional acrylates produce the most rapid curing but have several drawbacks if used alone: poorer solvent power for oligomers, inferior viscosity lowering ability, a tendency to leave high residual unsaturation in the final product, with its associated instability, and a tendency toward excessive crosslink density in the product, with resultant brittleness. Monofunctional monomers have a beneficial effect on the viscosity, flexibility, and adhesion, but react more slowly. Often the best compromise is secured by blends containing several monomer types [75,76]. A few typical acrylate monomers and their important properties are given in Table 9. Other examples include 1,6-hexanediol diacrylate, tetraethylene glycol diacrylate, and pentaerythritol triacrylate. A current catalog of the Sartomer Company (a subsidiary of the Atlantic Richfield Company) lists approximately forty monomers of varying functionality, nearly all acrylates and methacrylates [77]. Other companies, e.g. the Celanese Corporation, sell fewer kinds but in higher volume [78].

A difficulty associated with acrylate monomers is that many are skin and eye irritants. The corresponding methacrylates, in contrast, tend to cause less irritation. The most volatile monomers tend to be especially troublesome and it has been suggested that 2-hydroxyethyl acrylate, despite other good properties, is too toxic to be used [41]. A few nonacrylic monomers have been recommended, partly to alleviate toxicity problems. The most prominent are vinyl acetate and N-vinylpyrrolidone, both of which have fair reactivity [41].

TABLE 9

Important Properties of Some Acrylate Monomers

Monomer	Molecular Mass, g/mol	Functionality	Boiling Point, °C	Viscosity at 23 °C, mPa·s
Trimethylolpropane triacrylate	296	3	138 at 0.1 kPa	89
1,4-Butanediol diacrylate	198	2	120 at 1.3 kPa	4.6
2-Ethylhexyl acrylate	184	1	229 at 101.3 kPa	1.5
Hydroxypropyl acrylate[a]	130	1	60-65 at 0.13 kPa	10.7

[a] Commercial grades of this material usually contain a mixture of 2- and 3-hydroxypropyl acrylate.

Source: G. M. Jacobi, Verfkroniek 50, 75 (1977).

C Coating Formulations

The number of coating formulations given in the literature is too large to review adequately. Many are given in papers dealing with other aspects of curing, such as initiation. There are undoubtedly many more formulations that are proprietary and even in many published recipes the composition of oligomer(s) is incompletely known or not revealed. A few coating formulations are available [62] for Uvimer acrylated polyurethane compositions. One base composition, Uvimer 530, contains sixty percent oligomer and forty percent pentaerythritol tetraacrylate, has a viscosity of 375 to 600 poise, and yields a hard, glossy, brittle, chemically resistant resin. A clear resin included 100 parts of this mixture and 4 parts of benzoin butyl ether. A pigmented composition for electron curing on particle board consisted of the above 60/40 mix 51.5 parts, 2-ethylhexyl acrylate 5.0 parts, styrene 5.0 parts, titanium dioxide 15.4 parts, calcium sulfate 23.0 parts, and stabilizer 0.1 part. Other examples of compositions with high flexibility are Uvimer 765 and 775, which contain another urethane oligomer and the different diluents indicated in Table 10. These films are suggested for strapping tape, fabric coating, and paper coating. A few other acrylate-containing formulations are detailed in Table 11 [41,74,79]. Some ink formulations will be given later in the report.

One rather general difficulty has occurred in trying to duplicate coatings with very low viscosity, much solvent, and a high pigment-to-vehicle ratio [41]. A low-viscosity formulation can be made using the appropriate reactive diluent in large proportions, but when the diluent reacts it becomes part of the resin, therefore, the final film does not have the desired high pigment concentration. On the other hand, sufficient

TABLE 10

Two Uvimers: Their Composition and Properties

Formulation number	765	775
Composition[a]		
Urethane oligomer	52	67
2-Ethylhexyl acrylate	34	--
2-Hydroxyethyl acrylate	14	--
2-Ethoxyethyl acrylate	--	33
Properties		
Viscosity, Pa·s	2.2-2.7	1.8-2.2
Hardness, Shore A	68	90
Cure speed[b], cm/s/lamp	7.6	19

[a] In parts.

[b] On a 0.1 mm film using two 80 W/cm lamps and 3% 2,2-diethoxyacetophenone sensitizer.

Source: D. D. Perry, W. Rowe, A. Cirignano, D. S. Davis in "Ultraviolet Light Induced Reactions in Polymers," S. S. Labana, Ed., ACS Symp. Ser. 25, Am. Chem. Soc., Washington, DC, 1976, p. 150.

TABLE 11

Composition and Properties of Several Acrylate-Containing Coating Formulations[a]

Clear UV Curable Coating for Wood [1]		
Acrylated urethane	35	
2,2-Dimethylpropane-1,3-diacrylate	20	
2-Hydroxyethyl acrylate	20	
2-Ethylhexyl acrylate	13	
2,2-Diethoxyacetophenone	2	
Silica (flatting agent)	10	
Paper Overprint Varnishes [2]		
Acrylated oil (Synocure 3110)	47.2	0
Epoxy acrylate (Synocure 3100)	0	47.2
2,2-Dimethylpropane-1,3-diacrylate	47.2	0
Monofunctional monomer (Synocure 3165)	0	37.8
Vinyl acetate	0	9.4
Benzophenone	2.8	2.8
N-Methyldiethanolamine	2.8	2.8
Viscosity, Pa·s	0.12	0.16
Cure rate, m/min/80 W/cm lamp	7	4
White UV Curing Enamel [2]		
Epoxy acrylate (Synocure 3100)	51.00	
1,6-Hexanediol diacrylate	19.00	
N-Vinylpyrrolidone	2.02	
Ethyl p-dimethylaminobenzoate	2.02	
2-Chlorothioxanthone	0.20	
Titanium dioxide	25.63	
Texafor FP 43	0.13	
Pigment volume concentration, %	8.6	
Cure rate, m/min/80 W/cm lamp	3	
Bisphenol A Epoxy Diacrylate [3]		
Acrylated epoxy[b]	66.6	
1,6-Hexanediol diacrylate	28.6	
Benzophenone	2.9	
N-Methyldiethanolamine	1.9	
Pencil hardness	3H-4H	
Reverse impact, N·m	< 1.1	
Conical bend failure, mm	31.8	
MEK rubs	> 200	

TABLE 11 (continued)

Aliphatic Epoxy Diacrylate [3]	
Acrylated epoxy[c]	66.6
1,6-Hexanediol diacrylate	28.6
Benzophenone	2.9
N-Methyldiethanolamine	1.9
Pencil hardness	HB-F
Reverse impact, N·m	1.1-2.3
Conical bend failure, mm	19
MEK rubs	10
Aromatic Urethane Diacrylate [3]	
Acrylated urethane[d]	66.6
1,6-Hexanediol diacrylate	28.6
Benzophenone	2.9
N-Methyldiethanolamine	1.9
Pencil hardness	F-H
Reverse impact, N·m	3.4-4.5
Conical bend failure, mm	13
MEK rubs	200
Aliphatic Urethane Diacrylate [3]	
Acrylated urethane[e]	66.6
1,6-Hexanediol diacrylate	28.6
Benzophenone	2.9
N-Methyldiethanolamine	1.9
Pencil hardness	F-H
Reverse impact, N·m	7.9
Conical bend failure, mm	9.5
MEK rubs	200

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[a] Formulations in percent by weight.
[b] Diacrylate of bisphenol A diglycidyl ether.
[c] Diacrylate of a long-chain aliphatic diglycidyl ether.
[d] Reaction product of two moles of hydroxyalkyl acrylate, two moles of toluene diisocyanate, and one mole of diol.
[e] Reaction product of two moles of hydroxyalkyl acrylate, two moles of Hylene W (E. I. du Pont de Nemours and Co.), and one mole of diol.

Sources: [1] J. W. Prane, Polym. News 5(1), 36 (1978).
[2] K. O'Hara, FATIPEC Congr. 14, 485 (1978).
[3] W. G. Bayer, "A Review of Ultraviolet Curing Technology," Pap. Synth. Conf. (Proc.) of TAPPI, 1978, p. 167.

pigment to give the desired final ratio would result in a highly viscous material during application.

VI INFRARED, MICROWAVE, AND HIGH FREQUENCY CURING

These three methods of curing all rely on heating by electromagnetic radiation of varying frequencies. They require that the coating or substrate have a reasonable absorption of the radiation but also permit some degree of penetration at the frequency used. Unlike the situation in oven heating, energy can be absorbed directly in depth rather than by conduction into the interior from the surface of the material. The advantage of these methods over convective heating is that the intervening air need not be heated. It is estimated that of all the "radiation" methods, IR has the broadest potential base of use [43].

A Infrared Curing

Some industrial use of infrared radiation for the drying of paints has existed since at least 1942 [80]. Natural gas as well as electric units can be used, and laser beams have been employed experimentally on enamels [81]. The cost of IR sources is low relative to UV lamps. The energy consumption is twenty to fifty fold greater than EB and reported cure times are 15 to 30 s with substrate temperatures of 200 °F. More sparing use of IR can be made where rapid cure need only be sufficient to permit stacking followed by continued cure in the stack. Recent developments in the use of IR ink curing are reviewed by Vernardakis [82].

The IR sources all supply a mixture of wavelengths whose general range depends on filament temperature. Long wave IR (4 to 1000 μm) is readily absorbed by air and difficult to focus. It lacks penetration in ink films and only surface drying is achieved, even this requiring far longer times than medium wave IR (2 to 4 μm). In possible conflict with these well accepted assertions, two Japanese reviews [83,84] concentrate on the use of far infrared for curing and a Russian report [85] mentions optimum curing conditions over the range from 600 to 680 μm; however, the latter study was limited to the region of 600 to 1000 μm. Medium wave IR is important in the drying of inks and coatings because many of the organic materials used in formulations absorb in this range, although for thin films the radiation may penetrate into the substrate. Short wave IR (0.7 to 2.0 μm) is only slightly scattered by air and can penetrate thick films and substrates. Matching the output spectrum of the lamp used to the absorption frequencies of the ink or coating can sometimes promote efficiency in curing.

Short wave sources have tungsten filaments at 2200 °C in a quartz tube and have a rated life of 5000 hours. Gold or aluminum reflectors are used to direct the radiation onto the work [86]. Medium and long wave sources can have a filament design similar to this [86], but usually consist of panels of quartz [87,88], pyrex [89], or ceramic [90,91], or sometimes of grids rather than panels [87,88]. They are heated to temperatures of, for example, 1150 °F (620 °C) for a peak wavelength of 3.2 μm, 1380 °F (750 °C) to achieve a peak wavelength of 2.8 μm, or 1800 °F (980 °C) for a peak wavelength of 2.3 μm. The complete emission spectra of three different medium wave IR sources are shown in Figure 33 [92]. Several suppliers of short wave and medium or long wave sources are listed by Vernardakis in his review. Combinations of a short and a medium wave source are also marketed by the Thermogenics Corporation (Stamford, CT) under the name Multi-Wave [93].

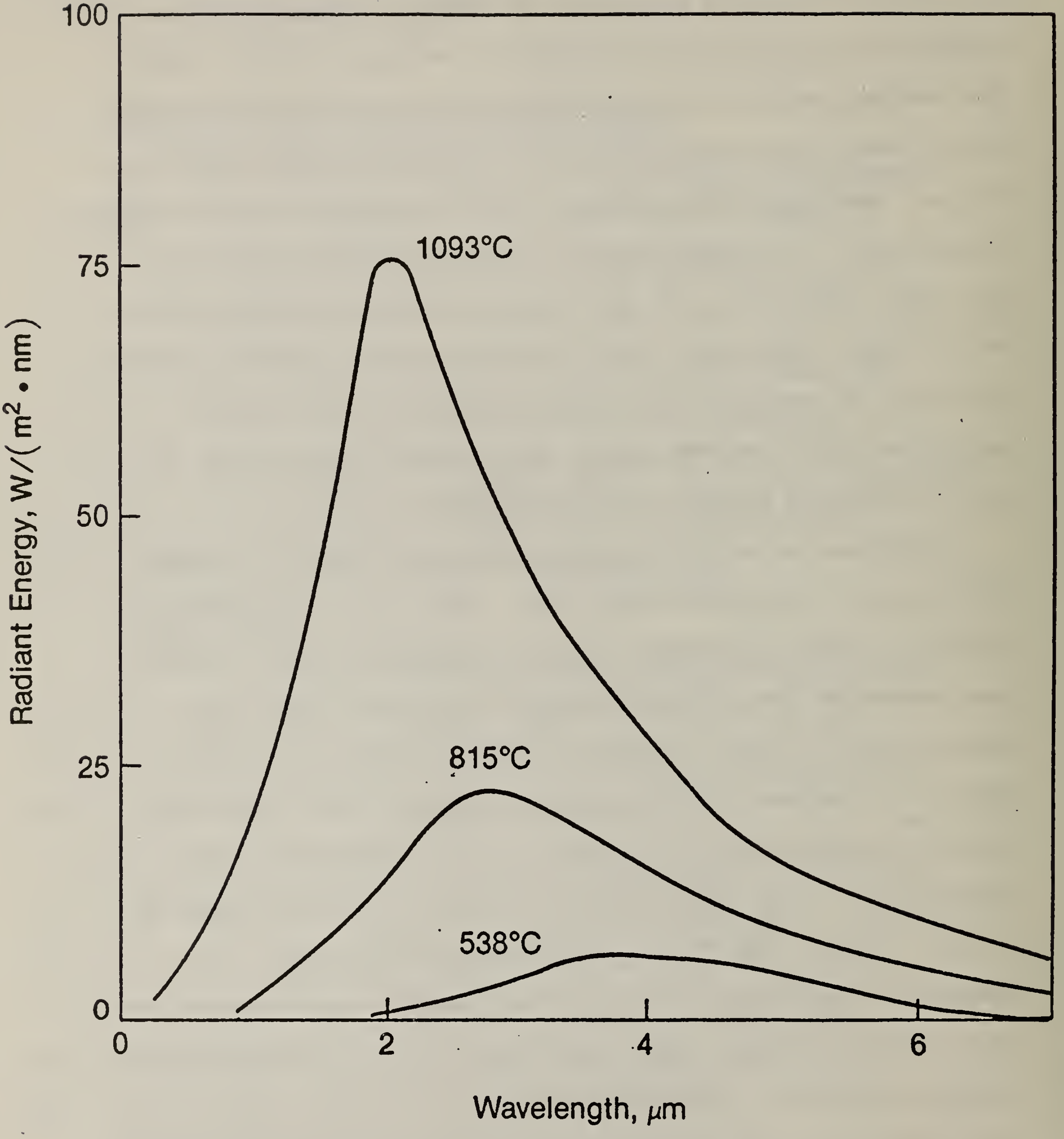


FIGURE 33 Infrared radiant energy distribution for several source temperatures.

The mechanism of action for IR curing depends on the type of coating or ink. Evaporation and lowering of viscosity or breaking of a gel to facilitate penetration into the substrate are both possible as is acceleration of crosslinking, however the latter is less likely. Tables have been prepared showing the IR absorption at major peak wavelengths for several polymeric materials that could occur in inks or coatings [93], and IR absorption traces for a resin and a solvent have been shown and compared with typical emission spectra of a short wave and a medium wave IR source [90]. The opinion has been expressed that short or medium wave IR is best for inks that dry by absorption into the substrate, and medium or long wave for inks used in color printing on webs, which dry largely by evaporation. Although conventional inks can respond to infrared radiation, special IR inks are also marketed, costing perhaps fifteen percent more than conventional [82,94]. This cost premium is, of course, very moderate compared to the approximately two hundred percent greater cost over conventional inks for UV and EB inks. Hashimoto suggests that future IR inks may contain "blocked" catalysts that become reactive only when subjected to intense IR [94].

B <u>Microwave and High Frequency Curing</u>

Microwaves, electromagnetic radiation over the range from 1 to 90 GHz, have been used experimentally to set coatings and inks but apparently not commercially to any great extent. One source indicates that "there has been little interest shown in recent years for microwave drying" [95]. This technique was used in Denmark for printing securities, on a web offset press in California, and for silkscreen printing in Germany [96]. Microwaves are also reported to assist UV curing [97], as will be mentioned in the following section on industrial methods of applying coatings.

One study of the microwave drying of inks [98] found that the dielectric loss characteristics of the ink solvent were of minor importance, in contradiction to reasonable expectations and occasional assertions [86,96]. Instead, in gravure and flexo film work, the substrate plays an important role. Microwaves were found to be a good way to dry and key, or promote adhesion of, heat resistant inks on an aqueous dispersion copolymer coated film substrate, otherwise difficult to print without embrittling the film. In another study, good results were obtained in the microwave drying of various films and papers coated with polyvinylidene chloride. This method was especially suitable for drying polyethylene film coated with an aqueous dispersion of polyvinylidene chloride without causing heat distortion of the film. The microwave drying was supplemented with air drying in this instance. Some attention has been given to the economics and energy consumption of printing with microwave technology [99].

Early work on high frequency curing of water-based inks employed radio frequencies in the VHF range, 100 MHz, where seventy-five percent of the energy was efficiently utilized to evaporate the water [100]. The loss tangent of the coating was found to decrease by a factor of about one-half as the fully cured state was reached in can coating applications [101]. One review mentions in passing the possibility of using ultrasonic curing in conjunction with other drying methods [102].

Polyethylene, a non-polar material, has been crosslinked by incorporating five percent t-butyl perbenzoate into the polymer at a temperature of perhaps 80 °C without appreciable decomposition of the highly polar additive, then applying 2.45 GHz microwave energy to cause thermal decomposition of the perbenzoate and subsequent crosslinking [103].

The decomposition products are less polar and less absorptive than the perbenzoate, therefore, the process is to some degree self-limiting and less likely to scorch the product. The possibility of molecular activation processes as the mechanism of perbenzoate decomposition is raised in this study. In other noncoating applications, microwaves and VHF have been used to vulcanize bulky rubber objects, principally because of their deep penetration and generation of heat in depth without the need for inefficient and slow conduction through the surface of the object [104-107].

VII INDUSTRIAL METHODS FOR APPLYING COATINGS

Radiation curable coatings have been applied by a number of the customary large-scale industrial processes [108,109]. Each process requires a coating material with unique characteristics and produces different finishes on the product, therefore, not all are adaptable for use with radiation curable materials. Some which have been employed successfully are described below.

Direct roller coating is fast and efficient, uniform if on a uniform substrate, and has no waste except material left at time of clean-up. Precision roller coating uses a knurled or engraved roll which meters a precise amount of material onto the application roll. This method improves flow of the base coat and eliminates "roping," or failure to level uniformly, which is sometimes seen in direct roll coating. Epoxy UV-curable coatings respond well to this type of application.

In curtain coating, the coating material is steadily pumped into an applicator head which produces a continuous vertical coating curtain that flows into a reservoir below. The part to be coated is passed through the curtain on a conveyor belt at speeds of up to 300 cm/s. The amount of coating applied is controlled by regulating the volume of material pumped into the applicator head and the speed at which the panel is fed through the curtain. Viscosity and temperature are two important parameters influencing the curtain coating process. A very uniform coating is applied independently of any variation in panel thickness. Acrylated urethane formulations are among those that can be applied [110]. Films thinner than 25 μm cannot be applied at all, and heating may have to be used to achieve the requisite low viscosity needed to produce any thin film. Also, a high conveyor speed is needed, which may be troublesome for light pieces.

Spray coating has been difficult to employ because of the loss of volatile monomers or reactive diluents that occurs during the process and the rather low formulation viscosity required. A few low-viscosity acrylated urethane formulations are said to have become available rather recently [110].

Problems can arise during or following application of radiation curable coatings. Difficulties with adhesion are fairly frequent and are often associated with coating shrinkage [41]. Many plastic surfaces require pretreatment by oxidation or electric plasma etching to insure proper adhesion of the coating. Some metal surfaces, especially tin and chromium, can also give improved adhesion with pretreatments. In pigmented coatings cured by UV, surface wrinkling can be caused by excessive cure on the surface and insufficient cure at the metal-coating interface due to light absorption and a strong cure gradient [50,56]. Any elastomeric machine parts, e.g. rollers, are much more likely to swell or react with acrylic monomers than with conventional vehicles and solvents. In many instances, some rubbers and polyurethanes are attacked while nitrile rubber, ethylene propylene rubber, and a polyvinyl chloride-rubber blend provide satisfactory service [95,111,112]. Companies furnishing the coating compositions can often recommend usable materials. One study has emphasized that UV curing may proceed very rapidly until the glass transition temperature of the coating, T_g, which increases with the degree of curing, reaches the cure temperature. At this point the coating vitrifies and curing ceases [113]. Further curing can be achieved by heating above the existing T_g. This suggests that, in general, hard brittle coatings cure better if some heat is applied. Several patents have been issued which describe processes in which microwave irradiation is employed as a method of providing this additional heating [97]. Infrared heating is another obvious possibility.

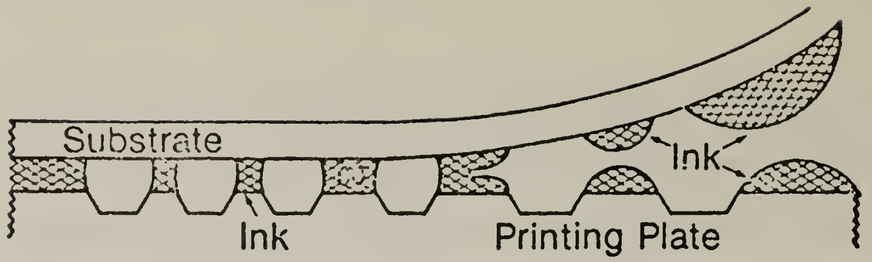
VIII UV AND EB CURING PRINTING INKS

A full and clear account of UV curable inks is given by Bean and Bassemir [114]; nothing important can be added to it on UV curing. It does not address itself to electron beam curing, however. In addition, long review articles [115-117] and several informative short reviews [58,69,86,94-96,111,118-120] are available on UV curing. Most of the considerations related to materials and radiation curing chemistry are the same for both printing inks and coatings.

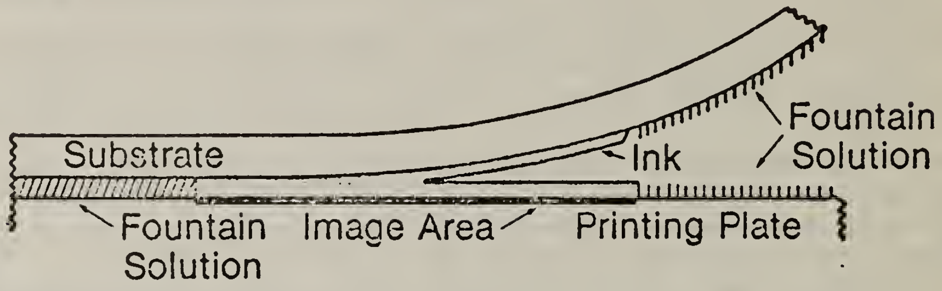
A Printing Methods

The major conventional printing methods differ widely and the range of ink properties needed varies enormously. These methods, given below, are also illustrated schematically in Figure 34 [114].

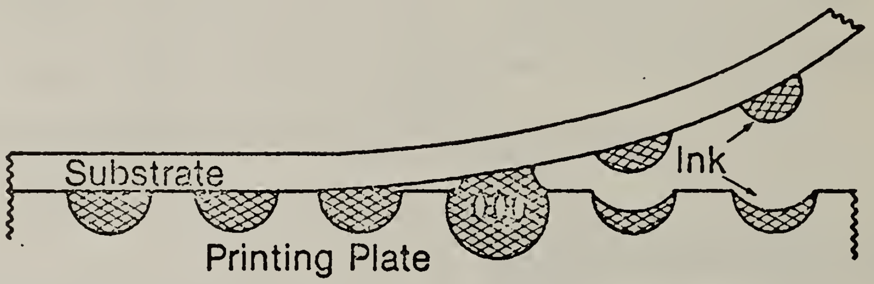
1 Typography (letterpress, flexography): A raised surface is inked and impressed against a substrate.



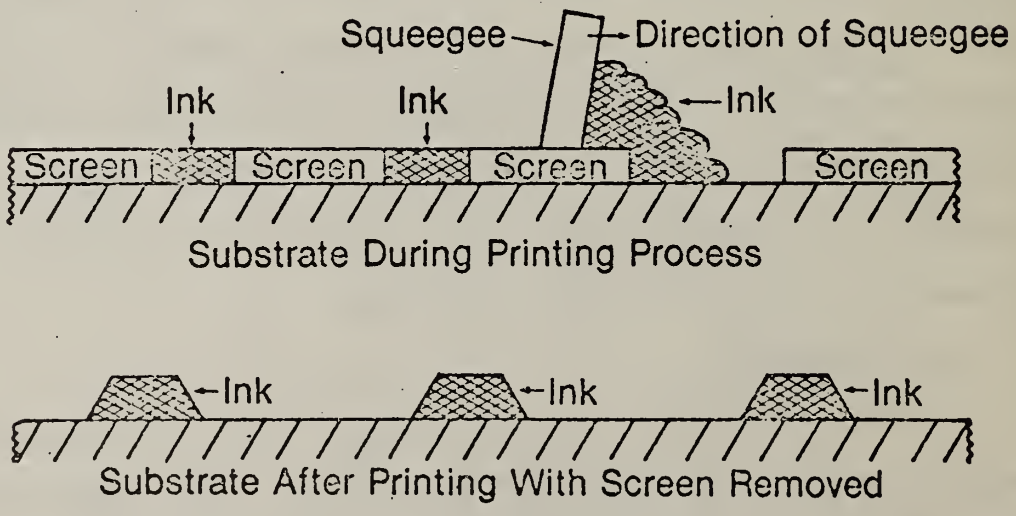
Typographic Printing



Planographic Printing



Intaglio Printing



Screen Printing

FIGURE 34 Schematic illustration of several common printing methods.

2 Planography (direct and offset lithography): The printing plate surface is flat. The image surface is hydrophobic and the blank surface hydrophilic. The plate is dampened with an aqueous "fountain solution" and then an inked roller is passed over the wetted plate. Ink transfers only to the hydrophobic image areas for printing.

3 Intaglio (gravure, steel plate engraving): The image areas are recessed below the plate surface. The plate is flooded with ink and then wiped, leaving ink only in depressed areas. After this procedure the plate is contacted with the printing substrate.

4 Silkscreen: The image areas are open areas in a fine screen while nonimage areas are blocked. Ink is pressed or squeezed through the open areas onto the substrate.

In all of these printing methods, except engraving and screen, the thickness of the dry film is much less than is achieved by ordinary surface coating, as indicated by the comparison in Table 12.

Some typical values of important ink properties, viscosity and pigment content (usually expressed as pigment volume concentration or PVC), are given in Table 13 [115] for various printing methods. In addition, more complex time- and shear-dependent rheological properties can be important, e.g. thixotropy and tack. Tack or cohesion must be sufficient for transfer to the substrate. On the other hand, excessive tack can interfere with the wiping of intaglio plates [121]. Lithographic inks in particular have peculiar problems associated with wetting properties. The ability to emulsify a small amount of water seems to be necessary but the ink must be basically hydrophobic, and a delicate balance of polar character is required. Too much surface active character

TABLE 12

Dry Ink Film Thicknesses for Various Printing Processes

Process	Film Thickness, μm
Letterpress	3- 5
Flexography	2- 4
Offset Lithography	2- 3
Rotogravure	5- 12
Engraving	12- 75
Silkscreen	12- 25
Most Surface Coatings	12-150

Source: A. J. Bean, R. W. Bassemir in "UV Curing: Science and Technology," S. P. Pappas, Ed., Technology Marketing Corp., Stamford, CT, 1978, p. 190.

TABLE 13

Typical Pigment Content and Ink Viscosity
for Various Printing Processes

Process	Pigment Content, %	Viscosity, Pa·s
Letterpress	20-80	1 -50
News Ink	8-12	0.2 - 1
Flexography	10-40	0.1 -10
Lithography	20-80	10 -80
Gravure	10-30	0.05- 1
Intaglio	---	up to 200

Sources: J. W. Vanderhoff in "Ultraviolet Light Induced Reactions in Polymers," S. S. Labana, Ed., ACS Symp. Ser. 25, Am. Chem. Soc., Washington, DC, 1976, p. 162; A. J. Bean, R. W. Bassemir in "UV Curing: Science and Technology," S. P. Pappas, Ed., Technology Marketing Corp., Stamford, CT, 1978, p. 191.

promotes "scumming," or the undesirable adhesion of ink to nonprinting areas. Many of the reactive monomers and amine initiator components used in radiation curing are more polar than their conventional counterparts, and careful formulation is necessary for their successful use in lithography. Tolerance for the usually either acidic (pH 4 to 5) or basic (pH 9 to 10) fountain solution is also necessary in these inks.

B Advantages and Disadvantages of Radiation Curing

The advantages of radiation curing depend upon the kind of printing process anticipated for use. Some conventional gravure inks contain thirty to sixty percent volatile solvent, which may dry rapidly by evaporation in an oven but requires solvent vapor disposal and may constitute a fire hazard. On the other hand, sheetfed offset inks dry by oxidation and emit very little solvent but often require several hours for complete drying in a stack after printing. In the first case, radiation curing eliminates the need for ovens and solvent vapor handling; in the second, it curtails the otherwise long curing time and obviates the need for anti-offset powder spray on the sheets before stacking. There is no energy savings for UV cured compared to sheetfed offset since the UV lamps require energy and the oxidative drying in stacks does not [122]. Besides production-line speed, an outstanding advantage of EB would be its utility for curing thick, heavily pigmented layers, such as might be encountered with intaglio or silkscreen work, where the UV cure rate would fall off intolerably with increasing depth of the ink layer. Stability on the printing machinery can be better than for conventional inks, as no drying need begin until radiation exposure, and cleaning requirements will also be reduced.

Some disadvantages of radiation curing should also be considered. Excessive UV light in the pressroom, except in the curing section, can cause premature curing on the equipment. Even bright daylight or fluorescent lamps may be a source of trouble. Rubber or elastomeric machine parts must be of compositions that resist swelling by the reactive diluents, as mentioned previously, or absorption and swelling of rollers or blankets may occur. This is especially detrimental because the resulting dimensional changes may alter the press settings. Desorption from rubber components into the ink is also possible, and ink contaminated by material from new rollers may be very slow to cure. The absence of a solvent to evaporate from radiation cured inks gives wet ink film weights and thicknesses that are smaller than usual. This can make application a delicate matter and result in a compressed tonal range for gravure printing. Rapid curing allows the ink films no time to smooth out before curing so gloss can be reduced. Because of the crosslinked character of the irradiated ink film, deinking and reclamation of waste stock are more difficult or impractical. Toxicity of initiators, catalysts, and reactive monomers and oligomers must also be taken into account.

C Ink Components and Formulations

The oligomers, monomers, and initiators (for UV applications) used are identical or similar to those found in coatings formulations. Bean and Bassemir [114] give compilations of these components as used in UV inks, with comments on some discontinued kinds. Among the monomers, hydroxypropyl and 2-hydroxyethyl acrylate are considered to be too great an irritant for use in printing ink. Other components are as in conventional inks: pigments (with precautions as to compatibility with UV curing monomers and oligomers) anti-mist agents, slip agents, antioxidants, wetting and dispersion aids, and sometimes small amounts of conventional modifying agents. Overall compatibility involves avoidance of dark polymerization in storage as well as noninterference with UV curing.

Bean and Bassemir also list a number of generic formulations for different ink types. Some may not be completely specified, and others may have been prepared from their personal experiences with the various print processes [114]. Some of these formulations are given in Table 14. Mixing and preparation steps during formulation ought to avoid high temperatures, bright light, and contaminants, and should be done in good contact with air, which acts as an inhibitor for most acrylate compositions.

D Equipment Requirements for Printing

Bean and Bassemir show several photographs of typical commercial UV curing attachments for printing equipment [123]. Retrofitting of existing printing machinery is said to be possible and not overly difficult except for sheet-fed offset printing apparatus [124]. Safety precautions principally involve protection from excess UV light, easily achieved but sometimes overlooked, and protection from irritant monomers and oligomers. Lacey and Keough have devoted a chapter to UV and EB safety considerations [125]. Some electron beam machines have been integrated into printing installations, at least experimentally [16,126, 127]. A schematic drawing of such a linear filament type unit is shown in Figure 35.

E Influence of Curing Parameters on the Printing Process

The theoretically derived dependence of cure speed on radiation intensity, initiator concentration, and coating thickness has been

TABLE 14

Generic Formulations for Several Ink Types[a]

Flexographic White	
Epoxy acrylate oligomer[b]	10.00
Diacrylate monomer	25.00
Monoacrylate monomers	25.00
Mixed photoinitiators	4.00
Amine accelerator	1.95
Inhibitor	0.05
White pigment	27.00
Adhesion modifying resin	6.00
Polyethylene wax	1.00
Letterset/Litho Sheetfed for Paper and Board	
Epoxy acrylate[b]	40.0
Polyol acrylate[c]	25.0
Trimethylolpropane triacrylate	3.4
Mixed photoinitiators	6.5
Inhibitor	0.1
Colored pigment	25.0
Tack at 6.67 Hz, 32 °C, 1 min	12-18
Letterset/Litho Web for Paper and Board	
Epoxidized soybean oil acrylate	30.0
Epoxy acrylate[b]	20.0
Polyol acrylate[c]	15.0
Trimethylolpropane triacrylate	2.9
Mixed photoinitiators	12.0
Inhibitor	0.1
Colored pigment	20.0
Tack at 20 Hz, 32 °C, 1 min	14-20
Letterset/Litho Overprint for Paper and Board	
Epoxy acrylate[b]	54.0-50.0
Trimethylolpropane triacrylate	30.0
1,6-Hexanediol diacrylate	7.9
Benzophenone	5.0
Amine accelerator	1.5
Inhibitor	0.1
Anti-mist additive	1-5 as required
Slip additive	0.5
Tack at 20 Hz, 32 °C, 1 min	8-12

TABLE 14 (continued)

Letterset/Litho Metal Decorating for Flatsheet 3-Piece Can	
Polyol acrylate[c]	30.4
Epoxy acrylate[b]	28.0
Resin modifier	14.0
Mixed photoinitiators	10.0
Inhibitor	0.1
Colored pigment	16.0
Tack reducer[d]	1.5
Tack at 6.67 Hz, 32 °C, 1 min	25-30
Letterset Metal Decorating for 2-Piece Can	
Polyol acrylate[c]	34.0
Epoxy acrylate[b]	25.0
Resin modifier	11.5
Mixed photoinitiators	9.0
Colored pigment	15.0
Wax	4.0
Tack reducer[d]	1.5
Tack at 20 Hz, 32 °C, 1 min	22-27
Packaging Gravure Red	
Epoxy acrylate oligomer[b]	10.0
Diacrylate monomer	35.0
Monoacrylate monomer	34.2
Mixed photoinitiators	4.0
Amine accelerator	1.7
Inhibitor	0.1
Red pigment	10.0
Adhesion modifying resin	4.0
Polyethylene wax	1.0
Silkscreen	
Epoxy acrylate[b]	20.0
Polyol acrylate[c]	10.0
1,6-Hexanediol diacrylate	20.0
Polyester resin	29.0
Benzoin isobutyl ether	5.0
Inorganic filler	10.0
Colored pigment	3.0
Flow agent	3.0

---

[a] Formulations in percent by weight.

[b] A variety of epoxy acrylates are commercially available. The most popular types are based on bisphenol A. The viscosity of these vary and this will regulate the ratios of oligomer/monomer/reducer required.

TABLE 14 (continued)

[c] There are many possible polyacrylates of this type. Perhaps the best known is pentaerythritol tri- or tetraacrylate or a modified version thereof.

[d] Many tack reducers have been recommended. These have been, typically, various plasticizers, high boiling alcohols, esters, ethers, and, in some cases, mono and diacrylates of low volatility.

Source: A. J. Bean, R. W. Bassemir in "UV Curing: Science and Technology," S. P. Pappas, Ed., Technology Marketing Corp., Stamford, CT, 1978, p. 200.

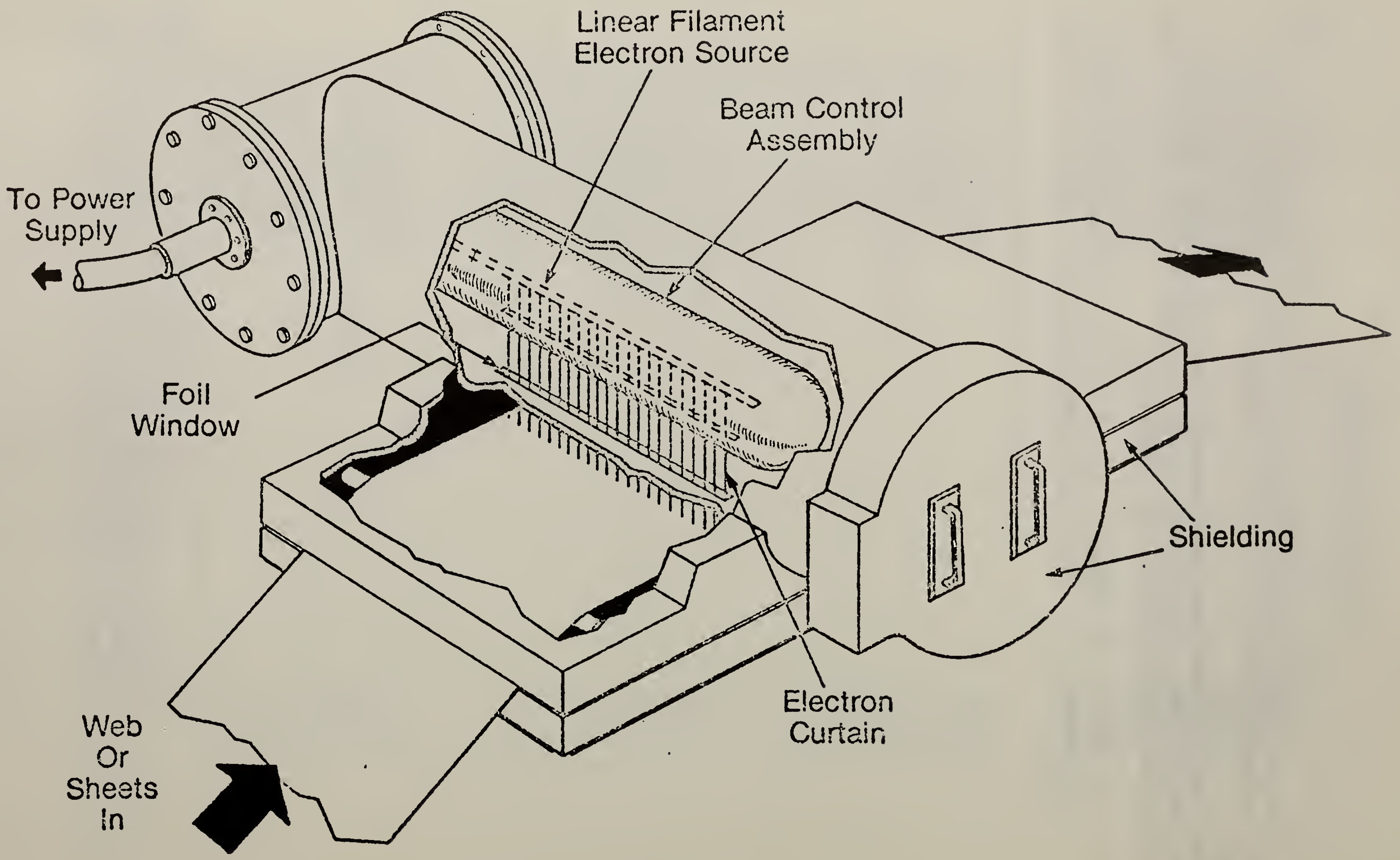


FIGURE 35 A linear filament electron beam printing installation.

considered earlier in this report. However, such ideal behavior is not easily achieved during the printing process. Lamp intensity has been found to change with distance in a complicated way; several maxima usually occur as the work approaches the lamp. In addition, the variation of cure rate as a function of intensity usually observed in practice is completely contrary to expectations from the simple theory of steady-state free radical chain reactions. In place of the expected simple relationship:

$$R \propto I^{\frac{1}{2}}C^{\frac{1}{2}},$$

where, as previously defined, R is the rate of polymerization, I the light intensity, and C the initiator or sensitizer concentration (see earlier discussion in Chapter II for derivation), one finds the very complicated empirical dependences of cure speed on intensity illustrated in Figure 36 [114]. In many instances, the intensity exponent is nearer to two than the theoretical value of one-half and is not always constant over the range of intensities. The UV screening effect of pigments involves obvious effects on the cure rate for different ink colors; this is also evident in the figure.

The variation of cure speed with initiator or sensitizer concentration also violates the simple equation just discussed. Empirically, the logarithm of photosensitizer concentration is often found to be inversely proportional to the time for cure as shown in Figure 37 for both clear and pigmented films [114]. The theoretical equation predicts that such semilog plots should not, in fact, be linear. Part of this contradiction is implicit in the tendency of high concentrations of sensitizer to screen light from deeper layers, as discussed earlier for coatings; part is perhaps also related to the distribution of wavelengths occurring in actual UV lamps, as opposed to the ideal monochromatic radiation source assumed

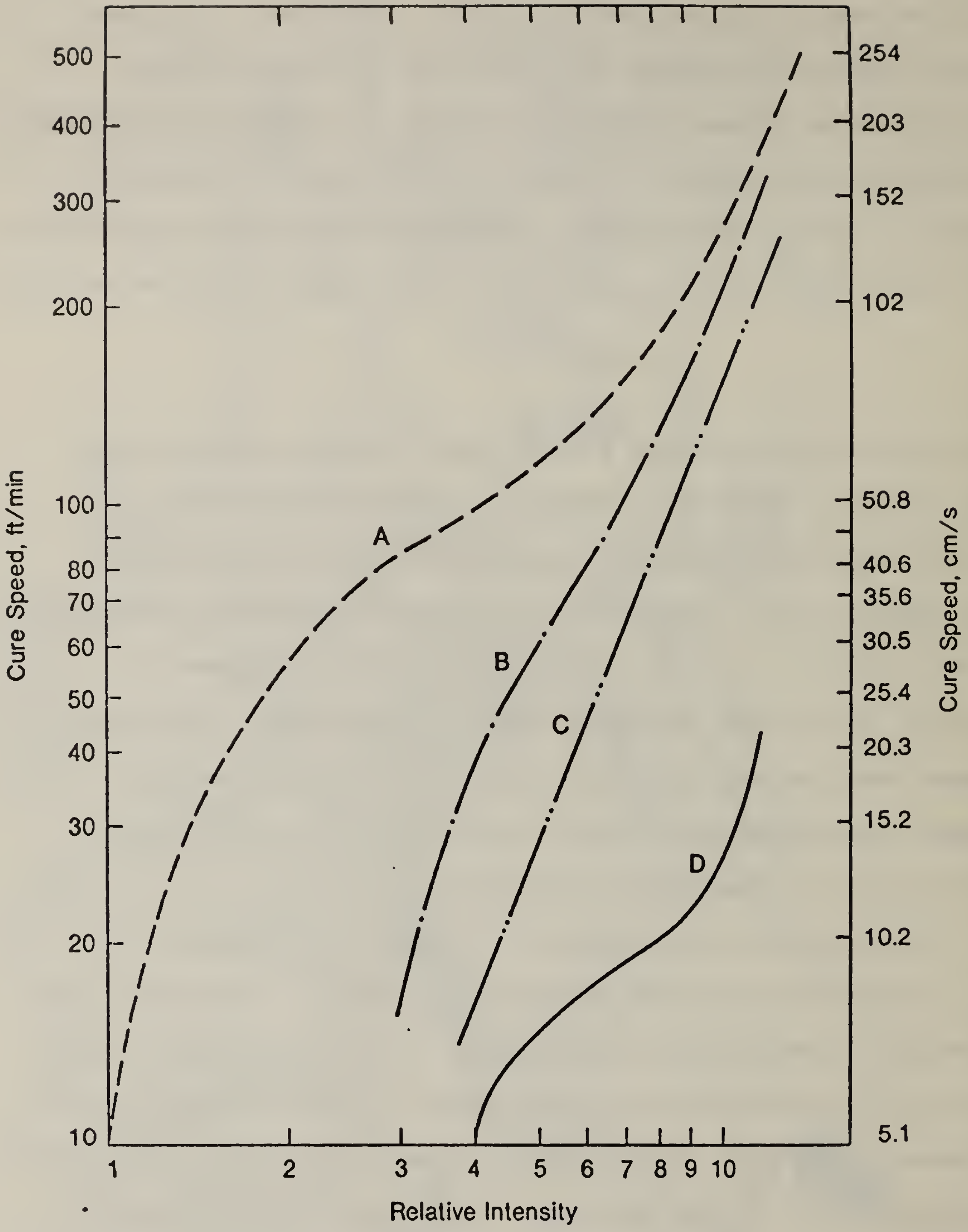


FIGURE 36 Cure speed per lamp versus light intensity for variously pigmented inks: A, magenta; B, yellow; C, cyan; D, black.

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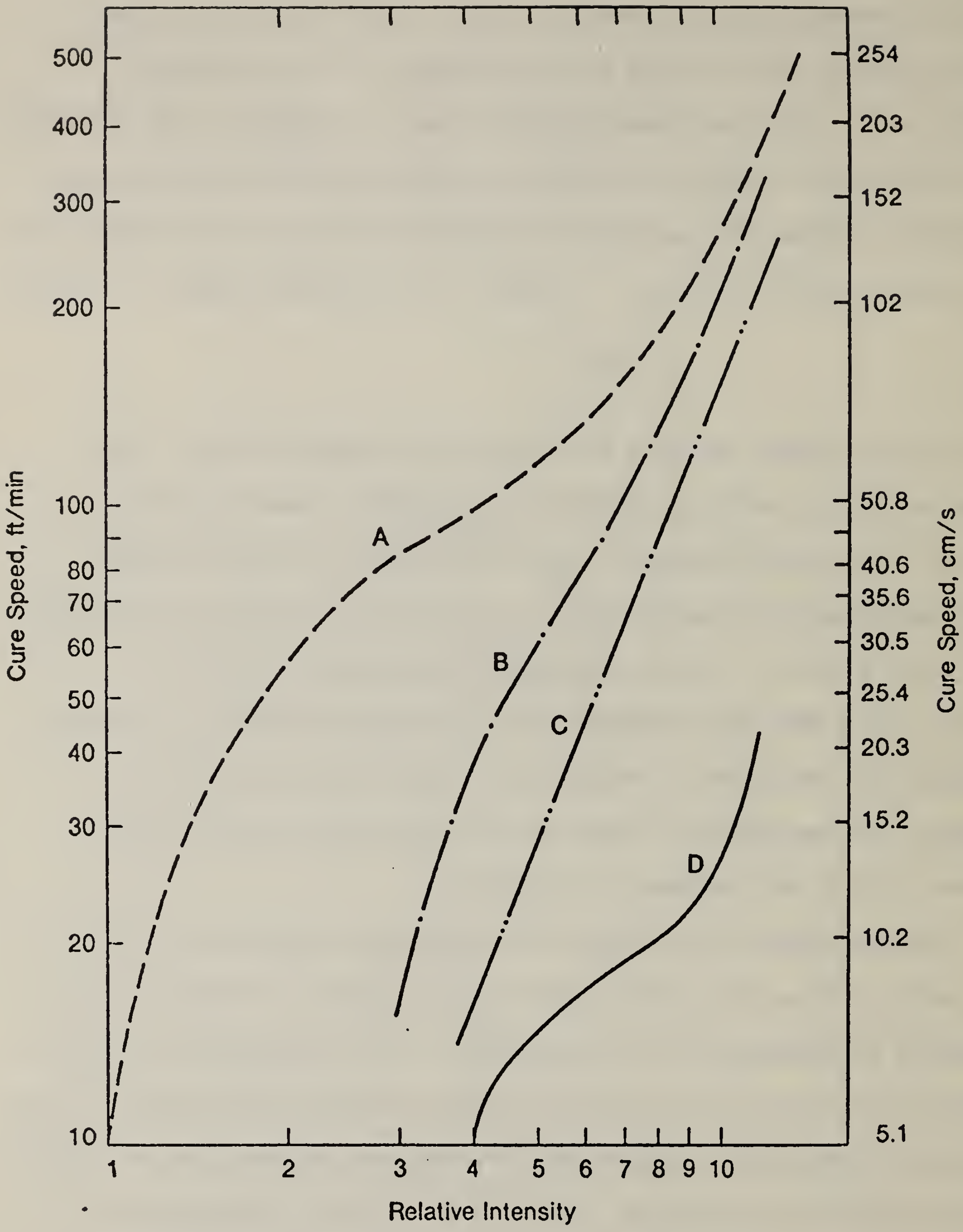

FIGURE 36 Cure speed per lamp versus light intensity for variously pigmented inks: A, magenta; B, yellow; C, cyan; D, black.

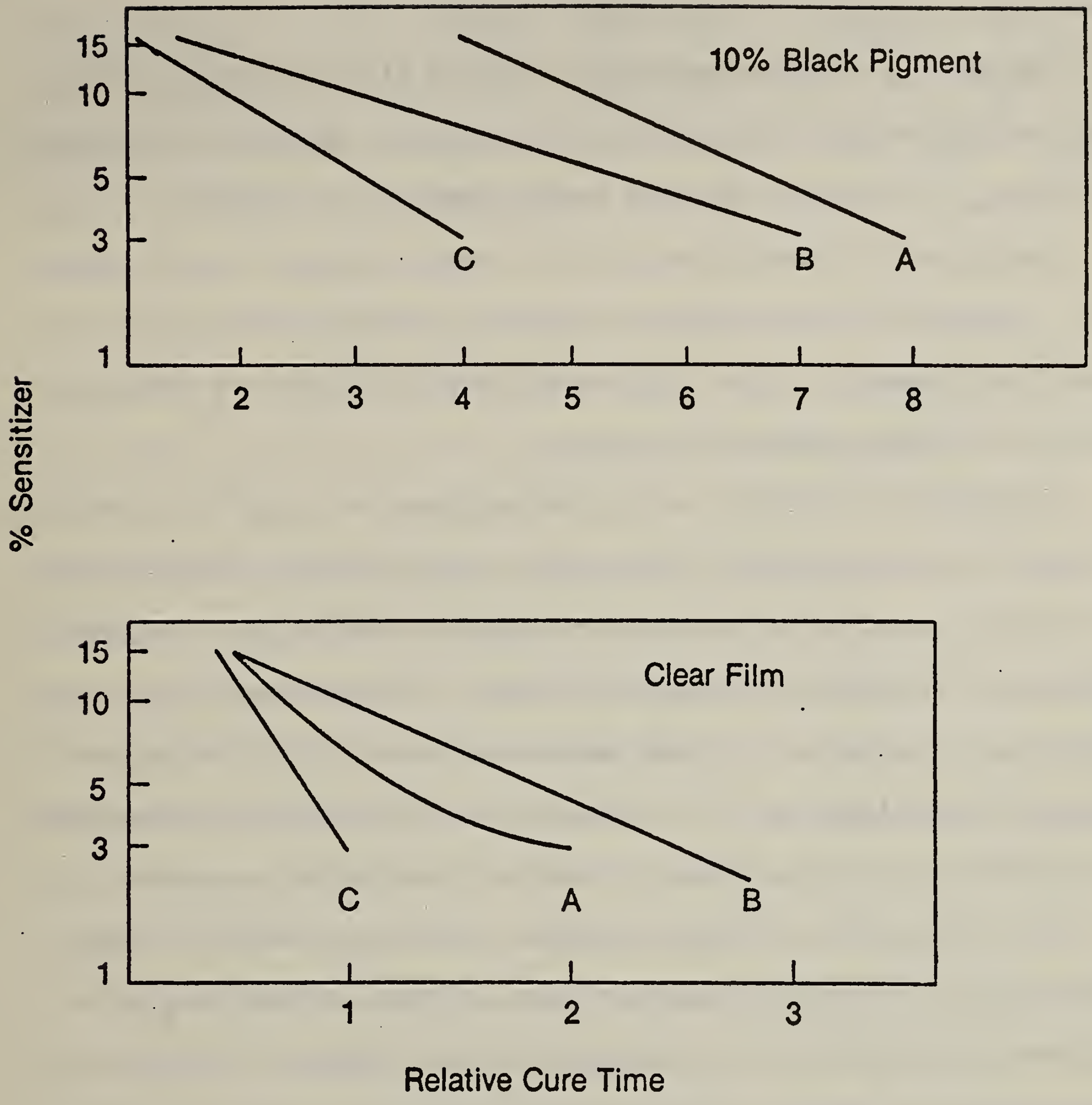

FIGURE 37 Relationship between cure time and sensitizer content for three unspecified sensitizers A, B, and C in clear and pigmented films.

for deriving the theory. The UV curing problems attributed solely to the presence of pigments in formulations have been previously considered in Chapter IV.

The decline of cure speed with increasing film thickness, which is rapid and occurs such that a plot of log cure rate against film thickness is linear, is in accord with the Lambert-Beer law as expected.

Increasing the temperature aids the completion of curing for paste inks. We speculate that this observation is compatible with the glass transition temperature effect discussed previously under the heading of industrial coating application methods.

Interactions of UV inks with printing plates are usually not serious if the plates are of metal. Copper may react with amine sensitizers and become less receptive to ink, but can be rejuvenated by acid treatment or protected with special pretreating solutions. Photopolymer plates are generally usable because of their extreme degree of cross-linking and consequent resistance to inks. However, their life may be shortened due to softening caused by sorption of some ink formulation components.

Cures on metal or plastic substrates tend to be slow, since the achievement of a practical degree of cure on these surfaces cannot be assisted by absorption of liquid ink into the substrate. Adhesion to such surfaces is likely to be poorer; this is correlated somewhat with the large degree of shrinkage that occurs during polymerization. Adhesion can be promoted by slower curing formulations, the use of specifically better adhering compositions (e.g. epoxy and urethane), and by appropriate surface preparation. Liquid inks are slower to cure than paste inks, in general, and may be of some utility in applications where adhesion needs to be improved. Some experience with ink adhesion to plastic containers and metal can stock has been reported [47,128].

IX OTHER RELATED APPLICATIONS OF RADIATION AND RADIATION CURING

Noncoating applications of radiation curing are equally significant, commercially. A process of major importance is the crosslinking of wire insulation by electron beam radiation [129-149]. The largest production volume is in crosslinked thin wire insulation made of polyethylene and polyvinyl chloride (PVC). Polyethylene can be used at a higher service temperature and PVC is given fair fire resistance by this process. A critical application for the latter is distributing frame wire for telephone company use [129]. The formulation for this application includes PVC, tetraethylene glycol dimethacrylate, and a stabilizer. Some early hardening occurs at a dose of 0.1 Mrad; other properties (hot modulus, etc.) improve at later stages of the process. In some of these uses, it is important that the insulation fail by charring when over-heated, like rubber, and not by melting, like nylon. Even a moderate degree of crosslinking improves performance under such conditions as soldering at close quarters. EB machines of the scanning type irradiate the wire, which is often passed through the beam several times in a figure eight pattern or with twisting to give good access of electrons to all sides of the wire. In some machines, the same purpose is achieved by a magnet which gives a reverse curve to the path of the electrons. Polyethylene will crosslink in this manner without additives, but crosslinking monomers of the acrylate type are often added to reduce the dose needed for crosslinking. Some foamed cable insulation is also crosslinked. Thick cable insulation can be crosslinked with higher energy electrons but a limit is apparently imposed by the tendency of the accumulated charge of trapped electrons to break through the insulation in discharges that create pinholes and other flaws. Other polymers capable of EB crosslinking include polyvinyl fluoride, ethylene-chlorotrifluoroethylene, chlorosulfonated polyethylene, and ethylene-propylene-diene copolymer [130]. It is common for the usual polymer stabilizers to inhibit crosslinking and themselves be destroyed in the process. Special stabilizer systems, undisclosed in the open literature, must therefore be used in these EB applications. Without them, aging at high temperatures can lead to rapid deterioration [130,131]. Despite the importance of radiation crosslinking, it does not account for as much as one-half of the crosslinked insulation market.

Other important forms of radiation crosslinked polyolefins and their copolymers include foam sheet [150,151] and shrink packaging film and insulation [152]. Crosslinking is not the only possibility even for shrink film, as carefully controlled orientation and temperature treatment followed by rapid chilling can be used to give acceptable final performance [153]. With EPM copolymers (ethylene and propylene, but no diene), the radiation efficiency of crosslinking is small but becomes practical if "activators" such as ethylene glycol dimethacrylate or triallyl cyanurate are added. Much more suitable is EPDM, EPM which contains diene termonomer units, and again using "activators," but except in low voltage electric cables it has not become a significant part of industrial practice [154]. Blends of polypropylene and EPDM require addition of a monomer such as trimethylolpropane trimethacrylate to avoid degradation during crosslinking [132].

It is technically feasible to vulcanize rubber tires by radiation, and the product is not inferior, but the economics are unfavorable. An exception may be the partial precuring of tire components with 1 to 3 Mrads of EB radiation before assembly and main cure. This improves the "green strength" enough to prevent damage during assembly. Tires made in this manner can use more of the less costly synthetic rubbers while giving performance equal to high natural rubber blends [155].

A permanent press process for fabrics used for many years involved not crosslinking but graft polymerization by radiation [156]. This has apparently been abandoned in favor of strictly chemical methods [157]. Many other textile processes employing radiation have been under development but have not achieved commercialization [158-160].

The coating of leather with UV or EB curable formulations has been investigated in the laboratory [161] but it is not clear whether such processes have found commercial acceptance.

UV and visible light curing are used advantageously in several dental applications: composite fillings and liquid bonding agents for anterior teeth, pit and fissure sealants, and orthodontic bracket adhesives. The overwhelming advantage is the unlimited working time, followed by rapid cure when the desired shape is reached. The light source, which can be of several types, is brought to the proper location in the mouth via fiber optic rods [162].

An important and profitable field for UV and other radiation processes is the preparation of plates for printing and "resists" for microelectronic device fabrication [163-169]. The word "lithography," given a special meaning here, is often applied to these operations. Visible light usually gives adequate resolution for printing plate production. Although UV is most often used in microcircuit fabrication, other kinds of radiation--electron beams, x-rays, and ion beams--could in principle allow a greater degree of miniaturization and are being investigated. The starting materials for lithography include some that crosslink by molecular stepwise reactions. An example of such a system is given in Figure 38. The

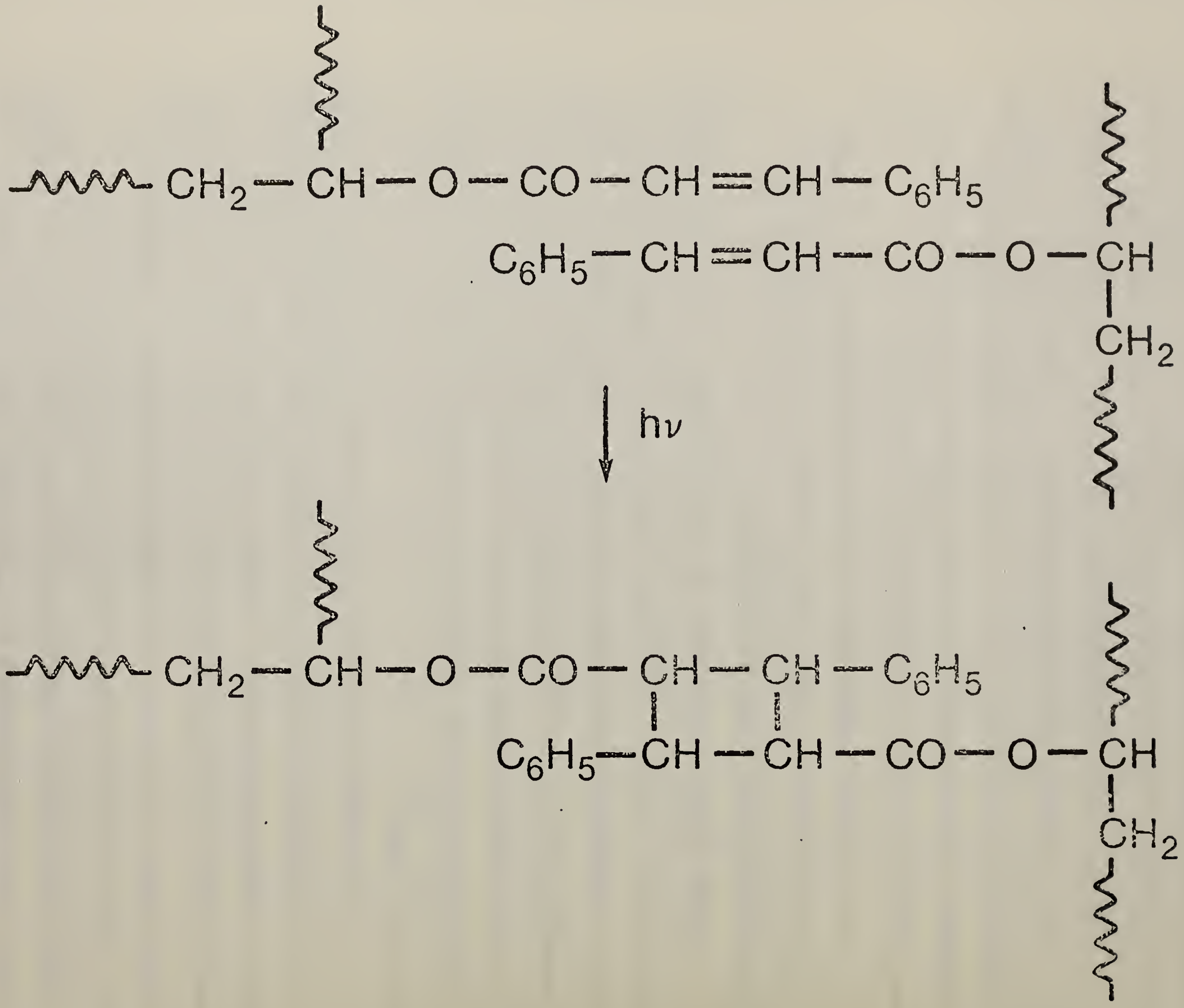

FIGURE 38 Molecular stepwise crosslinking reaction for systems used in microelectronic resist lithography.

substrate of the device is first coated with a radiation crosslinkable polymer. A "negative" resist is made by photocrosslinking, with an electron beam for example, the area to be protected from treatment then dissolving away the uncrosslinked material with an appropriate solvent. A fabrication step follows and involves etching or doping the now unprotected areas of the substrate while leaving the protected areas unaffected. Alternatively, a "positive" resist is made by degrading the polymer in the EB exposed area, removing it with a solvent, and etching or doping the area thus uncovered. Many of the lithography references cited are merely introductory or pertain to electronics manufacturing processes; Delzenne [163] and Tsunoda [164] offer the most comprehensive information on printing plate lithography.

As mentioned in the introduction to the report, some uses of radiation require the deep penetration that can best be accomplished with cobalt 60 gamma rays, despite the considerable inconveniences associated with their use. These processes include wood impregnation [170] and sterilization of prepackaged medical supplies [171]. A potential substitute for cobalt 60, having an advantage in that it could be turned off when not in use, might be developed in the future from the bremsstrahlung radiation from scanned electron beams of 4 to 5 MeV striking a suitable target [172].

X INDUSTRIAL RADIATION CURING APPLICATIONS: COSTS, EXAMPLES, AND STATISTICS

A General Radiation Curing

The most thorough market analysis of radiation curing, that of Barbier and associates [70], is based on data up to 1976, and only very fragmentary updating can be attempted. Cost estimates for different years are difficult to compare because of the effects of inflation and also because the share taken by capital costs is strongly influenced by interest rates, which have undergone large changes during the period of development.

The different radiation curing methods have widely varying capital equipment costs. The usual mercury-argon bulbs of 200 W/inch cost $250 each, and lamp and associated UV curing equipment costs are typically only several thousand dollars per production line. UV lamp life has apparently increased over the years, perhaps to on the order of 4500 hours for a 120 W/cm lamp [43], giving additional savings over earlier estimates. These figures can be compared to the cost of infrared bulbs which are usually only $100 each. Electron beam equipment costs were much higher, however, two hundred thousand to one million dollars per production line. The cost of UV and EB curable ink and coating materials was and is likely to remain roughly fifty to one hundred percent higher that conventional heat-set ink formulations [117].

It is well known that the energy cost per unit mass for conventional oven drying drops rapidly with increasing volume fraction solids in a coating formulation while, on the other hand, the quantity of oven heat required rises proportionally with substrate thickness. Energy consumption for UV coatings, per unit mass coating solids, drops rapidly as film thickness increases. Plots of the above relationships show that radiation curable coatings are competitive with solvent based coatings when the volume of solids in the latter is below thirty percent [173]. In UV curing, important cost savings are made by shifting from nitrogen to air for the blanketing atmosphere. The hourly utility costs in 1978 fell from $12.30 to $4.80 by eliminating nitrogen consumption for a 122 cm wide line with ten lamps operating at speeds of 50 cm/s.

As of 1976, the largest markets for materials cured by radiation were coatings and inks. The total consumption of radiation cured coatings in the U.S. was thought to be 4100 metric tons (t) for 1975; UV cured ink consumption amounted to 725 t during the same period. Table 15 gives a summary of their various uses and markets. Large scale commercial use of these materials began much earlier than 1976, however. The Continental Can Company, as early as 1972 for example, had eleven UV lines in nine plants for coating three-piece beer and soft drink cans [47]; the Adolph Coors Company had converted to UV from gas-fired lines by 1975 [174].

In 1979, the number of industrial electron beam machines was estimated at 230 and gamma radiation sources at 80, for a total of 10 MW power production and an estimated total product gross sales of more than $1 billion per year [157]. In 1981, the estimate had increased to 14 MW in EB machines and 1 MW in cobalt 60 sources [175]. The tendency is toward larger machines, capacity per device growing faster than the number of installations. The crosslinking of wire and cable insulation used a significant fraction of all EB capacity installed, one-quarter to one-third of the 7.9 MW EB capacity in 1977. The Western Electric Company alone in that year processed an estimated 1.8 billion meters of PVC wire so that it would resist satisfactorily the heat from soldering [176], but this amounted to only two percent of its total wire production. Japanese wire and cable processing by EB as of 1978 included twelve suppliers with twenty machines at 800 kW total power production [177].

Some of the earliest users of ionizing radiation, however, had dropped out of the field by 1979. They included Deering-Milliken, Incorporated, manufacturer of permanent press cotton by radiation graft

TABLE 15

Market Size for Actual Applications of Radiation Curing in 1975

Market or Submarket	Estimated Actual Market Size
Coatings (UV and radiation)	4100 t
Wood coatings	6.8 t
Containers, closures, metal decorating	320 t
Motor vehicles[a]	545 t
Inks (UV)	725 t
Packaging	567 t
Other printing	240 t
Sensitized printing plates	\$20,000,000[b]
Printed circuit boards	\$4,000,000[c]

[a] Calculated from volume usage statistics assuming a density of 1.44 kg/L.

[b] 2% of estimated total market size of \$1 billion.

[c] 10% of estimated total market size of \$40 million.

Source: M. Barbier, J. Vlahakis, R. Ouellette, R. Pikul, R. Rice, Electrotechnology (Ann Arbor, MI) 2, 29 (1978).

polymerization, and the Ford Motor Company, with operations in coating automobile parts. Reasons for the Ford decision to exit the radiation curing field included the relatively poor performance of the low solids EB curable coatings they used and the frequency of accidents related to the inert gas atmosphere employed [157].

Estimates are given by Barbier and colleagues [70] of the number of coating production lines for different radiation types and of possible future markets for these processes. They also give a market analysis for the Japanese radiation-cured coating and ink industry. Broad, qualitative summaries of various industrial radiation curing applications are given by Lacey [178]. These include: electric insulation, overprint coatings, bags and film, printed circuits, screen printing, wood finishing, and shrink tubing and shrink covers for fittings, flooring, and coating.

B Printing Inks

U.S. sales of UV inks and press varnishes over a recent three year period have been given by Bean and Bassemir and are listed in Table 16 [114]. These figures can be compared with the 1976 total of $0.7 billion for sales of all kinds of printing inks in the $37 billion per year graphic arts and communications industry, where printing ink usage could be subdivided as follows: 22 percent letterpress, 14 percent flexography, 31 percent lithography, 17 percent gravure, and 16 percent miscellaneous [116]. More recently, the volume of printing by various processes is given in 1982 as: 18 percent letterpress, 14 percent flexography, 45 percent lithography, 18 percent gravure, and 5 percent miscellaneous [179]. The fraction of letterpress printing is declining steadily while usage of lithography has increased considerably. In 1976, the share of the web offset printing market captured by UV inks climbed into the range of $4 to 5 million, mainly because of increased demand

TABLE 16

Estimated Sales of UV Inks and Press Varnishes

Market	Yearly Sales, millions 1975	 1976	 1977
Web offset	$3.0	$4.0	$3.0
Sheetfed offset	2.5	4.0	5.0
Metal decorating	1.5	3.7	5.0
Plastic decorating	---	0.3	1.0
Miscellaneous	0.5	0.8	1.0
Total	$7.5	$12.8	$15.0

Source: A. J. Bean, R. W. Bassemir in "UV Curing: Science and Technology," S. P. Pappas, Ed., Technology Marketing Corp., Stamford, CT, 1978, p. 188.

by magazine printers during a natural gas shortage. Much of this new usage ceased when the gas supply situation returned to normal as the costs for UV were too great to compete in the unperturbed marketplace. Since then, UV curing inks have been considered as specialty inks. In 1978, UV curable printing inks sales were estimated at $17 million in the U.S. and Canada [111]. Sales totaled from $5 to 6 million in the same year for UV lithographic inks and varnishes at the three dozen large sheet-fed installations, with perhaps a dozen major sheet-fed installations producing such items as record jackets and book covers. The metal decorating field amounted to $6 million in UV ink sales over the same period. One expert in the field has expressed the opinion that is is safe to project a healthy future for lithographic printing on foil, metal, plastic, and similar sheet-fed products [111]. Some very familiar consumer items printed by UV curing include: Kentucky Fried Chicken, Slurpee, Bufferin, and aspirin containers, Thermos ware, and most cottage cheese and yogurt containers.

The use of IR drying for sheetfed offset printing in the United States has been growing in the five years preceding 1980 [95], the most recent period for which figures are available.

XI ALTERNATIVE NEWER METHODS FOR NONRADIATION CURING

Methods other than radiation induced processes could also be used to avoid some of the curing problems of conventional inks and coatings. Among these alternative materials and methods are: modified heatset inks, nonradiation cured high solids coatings and inks, surface coated inks, water-based coatings and inks, catalytic two-part coatings, electrodeposition of coatings (mainly for metals), and exotic printing methods such as jet printing. These frequently offer appreciable advantages in reducing pollution or energy consumption. They are discussed in more detail in several references [86,95,115,119,180-182].

One type of high solids ink is a modified heatset ink using less solvent, perhaps only twenty percent as opposed to the normal forty percent, and containing no aromatics and a lower amount of paraffinic hydrocarbons in the solvent in order to diminish the air pollution burden. Such inks are called low-smoke, low-odor heatset inks. Their boiling point is often lower than the conventional inks, typically 104 °C (220 °F) rather than 135 °C (275 °F). Unfortunately for gravure and flexographic inks, reduction of the solvent content can hardly be done to any useful extent because of the low viscosity required for application.

Catalyzed high solids inks contain an acid-crosslinkable prepolymer (polyester-alkyd, urea-formaldehyde, or melamine-formaldehyde) plus a "blocked" acid catalyst. The activity of the acid, typically p-toluenesulfonic acid, is blocked during printing by either salt formation with ammonia, with amino groups of a prepolymer or additive, or by an ester moiety, but is later released by dissociation on the drying equipment at temperatures of 135 to 177 °C (275 to 350 °F) [183-187]. Some prepolymers, such as styrenated alkyds, can become reactive at drier temperatures without an added catalyst.

In a totally different kind of system, an oil-based ink may be covered while still wet with an oxygen permeable coating, such as alcohol soluble propionate resin or water soluble polyethylene oxide, and allowed to dry slowly beneath the protective coating. The covering eliminates setoff while still permitting a normal air cure.

Water-based paints and other coatings are well known, and experimental use has been made of water-based inks. The polymer is often of the acrylic type, and contains perhaps five percent carboxylic acid groups as comonomer units. These are generally neutralized with an amine to bring about varying degrees of affinity for water, or, in extreme cases, water solubility. The polymer may be present as a latex, a water solution, or a colloidal water-solubilized polymer that is sometimes supplied in alcohol solution but reducible with water. The latexes have rather low viscosity even at high molecular weight and may require an added water-soluble polymer to give the desired tack for many applications. These inks can be used in gravure and flexographic printing on absorbent substrates, but a disadvantage is their tendency to swell such substrates. Foaming and mold growth are two other possible difficulties.

Two-part systems have been used in Australia under the name Vapocure. The ink contains one reactant of the isocyanate type and, after application, the substrate is passed through a vapor bath containing an amine as the other reactant. A crosslinked resin is thus formed which presumably contains urea linkages. In some cases, a reactant such as ammonia vapor is sprayed onto the other component already applied on the substrate.

Two electrical methods have been used to apply coatings: electrophoresis from colloidal aqueous suspension and electrostatic powder spraying. Electrophoresis can be either anodic or cathodic. In anodic electrophoresis, polymer particles containing carboxylate ions migrate to the anodic substrate and are deposited on the metal by electrode reactions which form the uncharged carboxylic acid or its metal salt. Typically, an electromotive force of 150 to 250 V is applied for 60 to 90 s. Electrostatic powder spraying uses much higher voltages to apply a dry powder which is subsequently fused onto the metal substrate. In an example described, a wet oil-based varnish is first laid down in the printing pattern, the powdered ink is applied and the excess removed by electrostatic methods, and the remaining powder is then fused by heating.

The radically different method of jetset printing employs an array of nozzles a few micrometers in diameter, arranged in the pattern to be printed, to squirt a low-viscosity ink onto the substrate. Drying is commonly achieved by evaporating the aqueous solvent [188].

XII CONCLUDING REMARKS

The literature on radiation curing of printing inks and coatings has been reviewed. Radiation sources considered include electron beam, ultraviolet, infrared, and microwave. Other uses of radiation are also discussed briefly. Technical feasibility has been proven in a wide variety of applications, but early expectations of the near-complete replacement of conventional curing by radiation methods have not been realized, principally because of economic factors such as the less than anticipated severity of the fuel shortage, the probably irreducible higher cost of radiation curing materials, the high capital cost of electron beam equipment, progress in some alternative techniques, and occasional marginal difficulties with a few key properties such as adhesion. In special applications where decisive advantages exist, growth has been rapid and continues.

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The science and technology of curing organic materials with radiation is reviewed. Electron beam, ultraviolet, infrared, microwave, and high frequency radiation sources and the resin systems suitable for use with these sources are considered. Equipment necessary to affect a radiation cure is discussed and some practical problems unique to each radiation method are indicated. The application of radiation curing to industrial processes which employ inks and coatings is covered, with particular emphasis given to printing with radiation curable formulations. Included are discussions of the advantages and disadvantages of radiation curing inks, some typical ink components and formulations, the specialized machinery required, and the influence of parameters unique to radiation curing methods on the printing process. Other nonprinting but related industrial operations utilizing radiation for treating thin films and coatings are also considered. Some costs, examples, and market statistics are given for these commercial procedures. New nonconventional, but also nonradiation, alternative curing methods are discussed briefly. A bibliography of recommended further reading and a list of over two hundred fifty references are included.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Acrylates; crosslinking; electron beams; infrared; photocuring; photoinitiators; photopolymerization; polymerization by radiation; printing; reactive diluents; thermosetting resins; ultraviolet.

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