PB83-239566

Radiation Curing of Inks and Coatings

(U.S.) National Bureau of Standards
Washington, D.C.

Prepared for

Bureau of Engraving and Printing, Washington, D.C.

Jun 83

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR83-2722	2. Performing Organ. Report No. PB83-239566	3. Publication Date June 1983

4. TITLE AND SUBTITLE

Radiation Curing of Inks and Coatings

5. AUTHOR(S)

George A. Senich and Roland E. Florin

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

R-0101-02

8. Type of Report & Period Covered

Annual Report
10/1/81 to 9/30/82

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Bureau of Engraving and Printing
Department of the Treasury
14th and C Streets, S.W.
Washington, DC 20228

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.

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

USCOMM-DC 6043-

RADIATION CURING OF INKS AND COATINGS

George A. Senich and Roland E. Florin

Polymer Science and Standards Division
Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

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:

Polymerization

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

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

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

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:

$$\frac{d[R\cdot]}{dt} = k_1I[C] - k_4[R\cdot]^2 = 0$$

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

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

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:

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

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