Generic Scenario: Formulation of EB-Curable Coatings

Background

Radiation-curable materials are specially formulated materials that cure upon exposure to radiation. The most common sources of radiation used include ultraviolet (UV) and electron beam (EB). UV-curable coatings are more widely used than EB-curable coatings, in part because of the high capital investment costs associated with the EB curing systems. Both types of radiation-curable materials are used for coatings, inks, and adhesives. Many of these materials are manufactured and applied in much the same manner. However, EB coatings can be used to cure highly filled or pigmented formulations that cannot be cured by UV radiation. In EB coating formulations, the highly energetic electrons can initiate free-radical polymerization of the coating even in heavily pigmented systems [9]. Thus, EB-curable coatings typically are chosen for applications where pigmentation (color) is desired. For similar reasons, EB-curable coatings are chosen for applications requiring film thickness greater than 0.5 mil. EB-curable coatings are used for plastic, metal, wire, textiles, glass, wood, paper, no-wax vinyl flooring, fiberglass laminates, and release coatings. Precoated metal coils for white boards and appliances, clear finishes for wood, vinyl flooring, and automobiles are among some of the many applications in which these coatings are used [4,7,8].

Market

Much of the information on radiation-curable materials does not differentiate according to the formulated product (e.g., coating, ink, adhesive), but distinguishes markets according to the end use of the radiation-curable materials [1]. Thus, market share information often includes 'electronics' as a separate market for radiation-curable materials, as a relatively large portion of these materials are consumed by this industry.

In terms of dollars, the 1991 North American market for radiation curable materials, as seen in Table 1, has been placed at $250 to $300 million, or about 3% of the U.S. industrial coatings market in 1991 [3,4].

Table 1. Radiation-Curable Materials by End Use Category in United States [3]

End Use	1991 Market Share (%) Based on Dollar Value
Coatings	44
Inks	16
Electronics	32
Adhesives	4
Other	4

In 1990, an estimated 51 million pounds of radiation-curable materials were produced [2].

The dollar market for EB-curable inks and coatings in 1990 was estimated at $18 million dollars [5]. Based on the dollar market value for EB-curable coatings, the EB-curable market may be approximated as comprising 10% of the total radiation-curable market. This could be as much as 5.1 million pounds of EB-curable coatings produced in the United States in 1990.

The radiation-curable coatings market is currently experiencing rapid growth through an expanding variety of end uses. The annual growth rate is estimated to be between 10 to 20% by volume [3,4]. This growth has been

spurred by both economic and environmental considerations [6]. Radiation-curable coatings have the following advantages in production over conventional coatings:

- fast, almost instantaneous cure times that are desirable for high productivity and throughput on production lines
- low energy use because heat is not required to cure the coatings
- efficient use of plant space because large ovens are not required
- little or no solvent content, thus minimizing or eliminating volatile organic compound (VOC) emissions during coating operations
- eliminating of the high costs associated with the handling and disposal of the solvents, or solvent abatement systems.

EB Technology Description

EB curing is a chemical process that uses energy from accelerated electrons to polymerize and crosslink polymeric coatings. When electrons strike organic molecules, many bonds are broken. There can be dissociation, electron capture, electron ejection, or excitation [7]. The reactive species created initiate free-radical polymerization of the functionalized oligomers and monomers comprising the EB-curable formulation into highly crosslinked and chemical-resistant films. Cure is more rapid than attainable with UV curing systems, on the order of a fraction of seconds [7]. However, one drawback to using EB curing is that curing must be carried out in a nitrogen atmosphere because oxygen acts as a reaction inhibitor by scavenging the free radicals and preventing polymerization.

Electron beams used in EB curing usually are generated in commercial applications in self-shielding EB curing equipment. Potentials in the range of 150,000 and 300,000 volts typically are used. Energy transfer is very efficient, as most of the energy is transferred directly to the target materials without notable energy loss. Well-designed EB curing units transform approximately 90% of the incoming kilowatts of line power to electron beam energy [7,10].

EB Coating Formulation

Electron beam-curable coatings have three basic components:

- oligomers (25 to 90%)
- monomers (15 to 60%)
- additives (1 to 50%) [6].

Oligomers provide the cured coating with its basic physical properties. Oligomers usually are functionalized for EB-curable coatings by reacting with an acrylate such as hydroxy ethyl acrylate or hydroxy propyl acrylate [6]. The functionalized oligomers used most commonly are acrylated epoxy, acrylated urethane, acrylated polyether, and acrylated polyester. Functionalization with vinyl ether is growing in importance because of lower toxicity. Oligomers of epoxy-silicone and epoxy-siloxane also have been used. Each provides a different set of physical properties to the final coating.

Monomers are important in determining the coating viscosity, cure speed, crosslink density, and final surface properties of the film [6]. In terms of fast, clean polymerization, the order for choosing monomer systems tends to be:

acrylate > methacrylate > vinyl > vinylene > vinylidene > allyl [7].

Acrylates are the most commonly used monomers in current commercial systems, but as many as five monomers may be combined in a single formulation to balance cure speed and ultimate film properties. Vinyl ether monomers offer a less toxic monomer alternative for some applications [11].

Additives for EB-curable systems include pigments, fillers, dispersants, stabilizers, and dyes. Formulations may include up to 50% additives [6]. Because of the penetrating power of the electrons, highly pigmented, filled, or dyed systems can be cured in thicknesses of several mils [9]. Additionally, several layers of materials or coatings covered by other coatings can be cured simultaneously.

The following formula is representative of EB-curable clearcoats [5]:

•	oligomer	38%
•	monomer	58%
•	additives	4%
		100%

Manufacturing Process

The process for manufacturing EB-curable coatings involves blending the raw materials comprising the formulation into a precisely ratioed and homogeneously blended product [12,13]. Figure 1 illustrates simple batch process equipment. The formulation of radiation-curable coatings is a specialty market, so the batch sizes used during manufacture vary greatly from as few as 15 gal to of thousands of gallons [12,13]. Raw materials such as oligomers and monomers are supplied to the coatings formulator in liquid forms using drums or tankers, depending on the production capacity of the facility [13]. In some cases the oligomers and monomers are premixed by the raw material suppliers to meet the specifications of the formulators. In most cases these components are transferred directly to the mixing kettle using closed lines and pumps; however, in some operations a worker may pour the raw materials into the mixing kettle [12]. Preheating of the raw materials at 110 to 150°F sometimes is used to lower the viscosity of the components to facilitate transfer [13]. This will increase the vapor pressure of the raw materials.

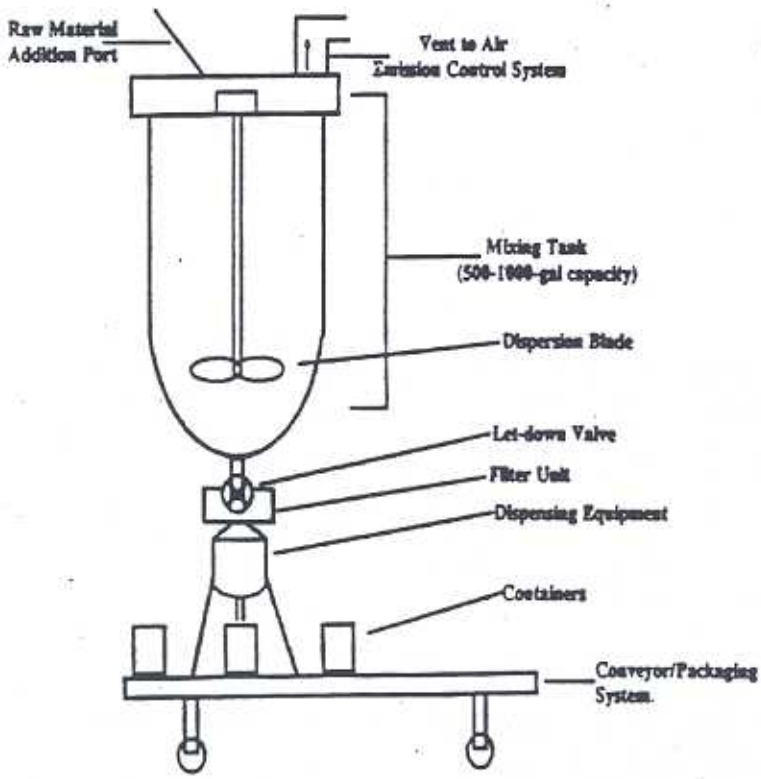

Figure 1. Schematic of EB-curable coating formulation equipment.

The oligomers and monomers are blended at low shear for a period of 30 minutes to 4 hours, depending on the size of the batch and the viscosity of the components [12]. The mixing kettle may be heated (110 to 180°F) to aid the blending process [13]. Mixing vessels are, almost without exception, closed systems [12,13]. After the oligomers and monomers are thoroughly blended, other materials such as the dispersion aids, stabilizers, and pigments are added to the blend. Most of the additives are in the liquid form and can be fed into the mixing kettle using pumps and feed tubes [12]. Pigments may be in the solid form. Mixing is continued to thoroughly disperse the additional materials. Heavily pigmented EB coatings and inks may require substantial mixing for thorough dispersion.

Once mixing is completed, quality assurance samples are drawn from the kettle for assessment [12,13]. Additional alterations to the formulation are made at this time. Once the formulation is considered satisfactory, the coating formulation is filtered using bag or cartridge-type filters to remove coarse impurities [12]. Finer filtration methods may follow for some specialty formulations. The end product is then fed into holding tanks or fed directly into containers for shipping. Shipping containers vary in size according to end use. Most products are supplied in 55-gal drums, totes (ca. 200 gal in size), or tankers [12,13]. However smaller containers are not uncommon, including 1- and 5-gal buckets, and even syringes [12].

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Waste Generation

The high cost of the raw materials used in radiation-curable coatings is an incentive to minimize waste in the manufacturing process. The yield of raw materials to product in the formulation of radiation-curable coatings is claimed to be well over 99% [12] due primarily to the closed-system method of manufacture and the low volatility of the raw materials comprising the formulation [13]. The sources of waste in the manufacturing process are

- residual raw material in storage containers
- residual coating in mixing tanks and lines
- coating deposited on filters during dispensing
- cleaning fluids
- spills.

Only a small percentage of the waste generated is residual raw materials remaining in packaging. Most of the waste generated is retained in the filters or remains as residual components in the feed lines and mixing vessels [12]. Filters typically are stored in drums and disposed of as hazardous waste. Feed lines and mixing vessels may be cleaned using solvents, water, or a monomer [12,13]. Manual scrubbing of the mixing vessels is necessary. Cleaning solutions typically are pumped into 55-gal drums and disposed of as hazardous waste [12]. The frequency of cleaning varies. Formulators making one type of coating, or coatings of similar formulations, clean only when the levels of contamination in their formulations are no longer within the tolerances set for their formulations. Formulators of specialty coatings, such as those manufactured for the electronics industry, may clean between every batch [12].

It is difficult to provide accurate industry-averaged data because this industry is in its infancy, facilities vary greatly in size, and many details concerning production volume and processing procedures are considered proprietary in the industry. The industry has a strong industry association that controls information about formulation and application of radiation-curable coatings. Currently, there are more than 100 formulators of radiation-curable coatings in the United States [12]. Information concerning the production capacity of these facilities, as well as the number of employees at each facility, varies markedly [12,13]. In some fully closed and automated feed systems, one worker may be able to run a complete batch processing line. However, the

following worker breakdown may be more appropriate when considering worker exposures on a given batch processing line [13]:

- 1 worker responsible for handling and raw materials, 1 shift per day, primary risk of exposure to raw materials
- 2 workers for setup and maintenance of mixing process, and packaging of formulations, average of 2 shifts per day, greatest risk of exposure to raw materials and formulations
- 1 worker for quality assurance, 1 shift per day, exposed primarily to formulations
- 1 worker for maintenance, 1 shift per day, periodic exposure.

Although some of the constituents of radiation-curable materials may be considered unfriendly, the formulation of these materials appears to be a relatively safe practice, due primarily to the facts that most of the transfer and processing steps take place in a closed system and the vapor pressure of the raw materials is very low [13]. In addition, due to the nature of some of the components of radiation-curable formulations, safe worker practices, proper clothing, and engineering controls usually are strictly enforced. Elephant trunks, hooked into local exhaust ventilation systems, typically provide ventilation at the emission points. The acrylic monomers used in the formulations usually are considered to pose the most threat to workers. OSHA currently defines the legal allowable air concentration, i.e., the time-weighted average (TWA), to be 25 ppm for ethyl acrylate, 10 ppm for methyl acrylate, and 100 ppm for methyl methacrylate [13].

Because of the great variety of radiation coating formulation facilities, it is not possible to devise a 'typical' formulation facility from which environmental releases and exposure levels can be extrapolated effectively without site-specific information. Nearly 100 sites now formulate some quantity of EB-curable coatings and could rapidly increase production volumes if demand were to increase. Generic equations are given below from which appropriate calculations can be made with some limited input from the manufacturer, direct observation of physical facilities, or information concerning coating production per unit time. Assumptions are presented when appropriate. A 1,000-kg basis is used for example calculations. Most calculations are done on a per site basis.

Variables/Assumptions

- PMN: F_{PMN} — weight ~~percent~~ fraction of PMN material is formula specific, given by manufacturer or estimated based on the role of the PMN in the formulation; i.e., if PMN is an oligomer it could be used at percentages as high as 90%.
- BS: $SIZE_{batch}$ — average batch size (kg); assume 1,000-kg basis
- NB: N_{batch} — number of batches produced per shift; assume 2
- NS: N_{site} — number of sites using PMN material could be from 1 to 100
- H: T_{shift} — 8-hour shifts
- Sh: N_{shift} — 2 shifts per day
- DOP: $T_{production}$ — 250 days of production per year
- IR: $RATE_{breathing}$ — worker breathing rate (m^3/hr)
- CR: $C_{respirable\ constituents}$ — concentration of respirable constituents in the air (mg/m^3)
- P: VP — vapor pressure of the PMN at room temperature (mmHg)
- MW: MOLW — molecular weight of the PMN material
- TR: $N_{transfer}$ — number of transfer operations per day involving PMN material; for calculations assume that one transfer results in exposure for the entire day. 16 hrs?

$\left(\frac{2\ shifts}{day}\right)\left(\frac{8\ hrs}{shift}\right) = \frac{16\ hrs}{day}$

Production of EB Formulations (kg/site year)

Generic: PMN × BS × NB × Sh × DOP = ??(kg/site year)

PMN × (1000 kg × 2 batches × 2 shifts) = PMN × (4,000 kg/site day)

$\frac{kg}{batch}$ $\frac{batch}{shift}$ $\frac{shift}{day}$

PMN × 4,000 kg/site day × 250 day/year = PMN × (1×10^6 kg/site year)

So PMN × 10^6 kg/site yr = Production of EB Formulations

$\left(\frac{kg}{batch}\right)\left(\frac{batch}{shift}\right)\left(\frac{shift}{day}\right)\left(\frac{day}{yr}\right)$

If volume of PMN produced is desired, divide the weight produced by the density of the PMN. If production of PMN desired assuming use by all U.S. producers, multiply the percent PMN by the 1990 annual production of EB curable coatings, or 5.1 million pounds (2.3×10^6 kg).

Environmental Releases (kg/site day)

Solid Waste: If the PMN material is in solid form, assume 1% of the PMN remains in packaging container and will be disposed of in raw form as solid waste.

Generic: $(0.01 \times \text{PMN}) \times \text{BS} \times \text{NB} \times \text{Sh} =$??(kg/site day)

$(0.01 \times \text{PMN}) \times 1000 \text{ kg} \times 2 \text{ batches} \times 2 \text{ shifts} = \text{PMN} \times (40)$ kg/site day

Liquid Waste: Assume 1% of product is generated as liquid waste. Some waste may be generated as residual PMN materials are left trapped in their packaging. Some liquid waste comes from water and other solvents used for cleaning. Regardless of the form, liquid waste will be determined as 1% of the total product. This waste may be in a form that can be cured to an inert solid form, or it may be necessary to store the waste in drums and dispose of it in its liquid form as hazardous waste by incineration.

Generic: $\text{PMN} \times \text{BS} \times \text{NB} \times \text{Sh} \times 0.01 =$??(kg/site day)

$\text{PMN} \times 1{,}000 \text{ kg} \times 2 \text{ batches} \times 2 \text{ shifts} \times 0.01 = \text{PMN} \times (40)$ kg/site day

Water Emissions: Normally no water emissions are generated. Small amounts of water or liquid are contained and disposed of as hazardous waste. For a worst-case estimation, use the PMN content of the liquid waste calculated above.

Air Emissions: Due to the low vapor pressure of the constituents of radiation-curable coatings, air emissions are expected to be negligible.

Worker Exposure (mg/day)

Most of the raw materials comprising radiation-curable coatings are supplied in the liquid form. However, as some of the additives (typically pigments) may be provided as powders, exposure-level calculations are provided for both solid and liquid PMN materials. Exposure levels are determined for 1 worker working one 8-hour shift in a given day.

Inhalation Exposure: For general in-plant inhalation exposure, the primary inhalation threat will be in the form of liquid vapor from the formulated coating. Most of the components of radiation-curable coatings have very low vapor pressures and are considered nonvolatile liquids. If the PMN is a volatile liquid, the vapor pressure (P) must be supplied by the manufacturer or estimated from known vapor pressures available in published literature to allow calculation of the concentration of respirable constituents in the air (CR). An inhalation rate of 1.25 m^3/hr is assumed [14].

Generic: $\text{PMN} \times \text{CR} \times \text{IR} \times \text{H}$ × N 8.0 = ??(mg/day)

Next, the production of radiation-curable coatings involves the transfer of liquids and solids to the mixing vessels. These operations pose a periodic threat to the workers performing these operations. Inhalation of liquids depends on the volatility of the liquid agent (assumed to be the PMN). The vapor pressure of the PMN can be used to calculate the concentration of the PMN in the air that might be expected during transfer from a 55-gal drum to the mixing vessel [14]. This is a worst-case approximation that assumes open-system manual feeding. The transfer frequency is assumed to be one, as a single contact is expected to result in exposure for the entire workday. Then, inhalation exposure during the transfer of liquid PMN material can be determined as:

$\left(\frac{mg}{m^3}\right)\left(\frac{m^3}{h}\right)\left(\frac{transfer}{day}\right)\left(\frac{exposure}{transfer}\right)$ 16 hrs/day unless T shift = 4-hrs

CR(PMN) × 1.25 m^3/h × 1 transfer per day × 8 hours per day = ??(mg/day)

In some instances, the PMN materials may be in powder form that poses an inhalation threat when added to the mixing vessel. In this instance the respirable dust should be considered to be comprised of 100% PMN. Total respirable dust exposure (15 mg/m^3) should be used. Therefore, inhalation exposure during the transfer of powder PMN material can be determined as:

15 mg/m^3 × 1.25 m^3/h × 1 transfer per day × 8 (hours exposure per transfer) = ??(mg/day)

Dermal Exposure: Dermal exposure is limited to incidental exposure during transfer materials handling. This includes handling liquid and solid raw PMN materials used to formulate the coating, and exposure to the coating product containing the PMN during transfer of the product to containers for shipping. Exposures are limited to contact with the materials during transfer operations. TR is assumed to be one, as a single contact is expected to result in exposure for the entire day. Equations approximating exposure levels are based on data compiled on contact operations as given CEB (1991, Table 4-13)[14].

Liquids: (1,300 – 3,900) mg/m^3 × TR × PMN/100 = ??(mg/day)

Solids: (6,500 – 18,200) mg/m^3 × TR × PMN/100 = ??(mg/day)

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