Generic Scenario: Roll Coating of Electron Beam (EB)-Curable Coatings

Introduction

Roll coating is a coating application method that uses an elastomer-covered steel roller to transfer a coating to a flat substrate moving past the roller [11]. This efficient process, very similar to printing, is capable of applying a thin, well-controlled coat of paint at very high speeds [11]. Roll coating is a popular coating method for both ultraviolet (UV) and electron beam (EB) radiation-curable coatings, as this method of application can be used to coat flat stock products at rates exceeding 1,000 ft/min [8]. Its advantages are that continuous feedstock can be rewound immediately, space is conserved by the elimination of oven passes, and volatile organic compound (VOC) emissions are negligible or nonexistent.

Market

Much of the market information on the use of radiation-curable materials does not differentiate according to radiation type (UV or EB) or formulated product (e.g., coating, ink, adhesive), and little market share information is reported based on the application method. However, Table 1 shows one estimate of the electron beam operating units used in the United States in 1992 (5).

Table 1. EB Operating Units: Current Status In United States

Use	Existing Units	Planned Adds	Totals
Ink	14	8	22
Coatings	4	9	13
Totals	18	17	35

In terms of dollars, the 1991 North American market for radiation-curable materials has been placed at $250 to $300 million, or about 3% of the U.S. industrial coatings market in 1991 [3,4]. As seen in Table 2, based on dollar value, coatings accounted for 44% of 1991 market for radiation-curable materials; inks, 16%; electronics, 32%; adhesives, 4%; and other end uses, 4% [3].

Table 2. Radiation-Curable Materials by End Use Category in the United States

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

It is estimated that 51 million pounds of radiation-curable materials were produced in 1990 [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.

The radiation-curable coatings market currently is 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:

- Their fast, almost instantaneous cure times are desirable for high productivity and throughput on production lines.
- They use little energy because heat is not required to cure the coatings.
- Plant space is used efficiently because large ovens are not required.
- They have little or no solvent content, and thus minimize or eliminate VOC emissions during coating operations.
- They eliminate the high costs associated with the handling and disposal of solvents, or solvent abatement systems.

Due to the fast cure speed of EB materials, EB-curable coatings often are applied by roll coating. Roll coating can maintain production rates as high as 1,000 ft/min for coating flat stock products (10). EB coatings on paper webs can be cured at a rate of 1,300 ft/min [9]. The fast line speeds possible with EB curing can increase production capacity so that the extra capital equipment expense required by these systems can be justified.

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]. Although not all roll coating uses EB-curable coatings, some information on the potential market size can be inferred from industry figures. One source estimates that the major appliance white good industry (refrigerators, freezers, washers, dryers, and ranges) paints from 600,000 to 700,000 tons of metal a year. Of this amount, about 130,000 tons are prepainted by roll or coil-coating processes and another 376,000 to 436,000 tons could be prepainted [4]. The automotive industry also could use roll or coil prepainting technology more extensively than currently practiced.

Technology Description

Roll-coating methods for EB-curable coatings include both direct roll coating and reverse roll coating [13]. In direct roll coating, sheet stock materials are fed between two rollers, and coatings are applied using an applicator roll rotating in the same direction [11]. Reverse roll coating (commonly referred to as coil coating) can be used to coat less rigid materials such as sheet metal or paper. Roll-coating by this method is the fastest and most economical of the two roll-coating techniques. In this process, the applicator roll runs in a direction opposite the feedstock, which is fed directly from a coil of uncoated material.

Both of these processes use an applicator roll to apply the coating, a feed roll (or pickup roll) to supply coating material to the applicator roll, and a pickup roll to supply coating to the feed roll [11]. The pickup roll is partially submersed in a tray containing the coating material. With both methods, coatings can be applied to both sides during one pass if an additional set of applicator rolls is used. New coating material is supplied to the feed trough only when required to maintain the continuous coating process. Coatings usually are supplied using feed lines, but may be manually poured in some smaller operations [14]. Excess coating material not adhering to the feedstock is redirected to the feed trough for recycling. To maintain product quality, the environment where the roll coating is being performed usually is controlled and personnel access is limited [15]. Figure 1 shows a flow diagram for a roll-coating line.

Once the coating is applied, it is conveyed to the EB curing stations where the formulation is fully cured to impart the physical properties to the applied finish. EB curing is a chemical process that uses energy from

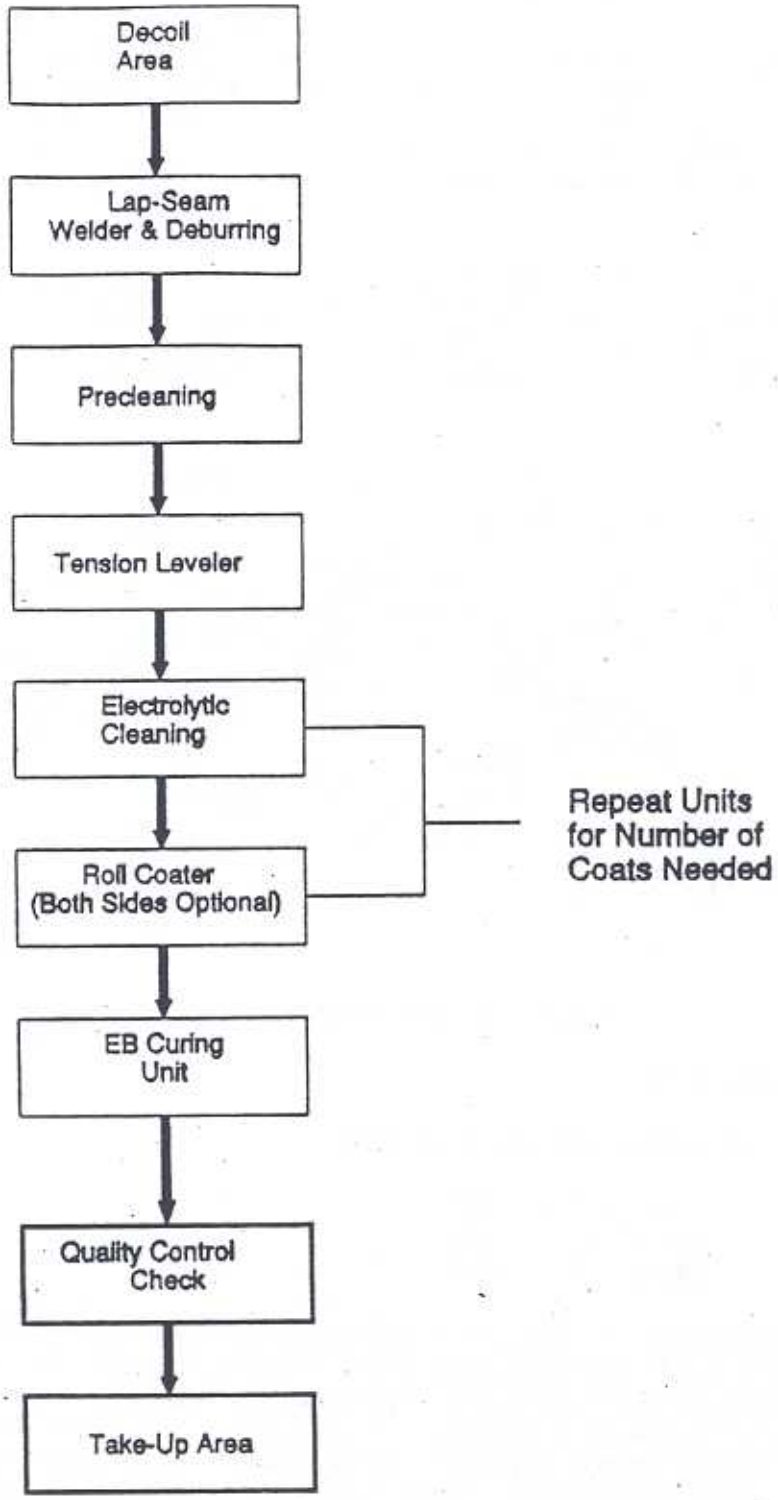

Figure 1. Flow diagram of roll-coating line for EB-curable coatings

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 [6]. The reactive species created initiates 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 (fractions of a second) than cure with UV curing systems [6]. EB curing must be carried out in a nitrogen atmosphere because oxygen acts as a reaction inhibitor by scavenging the free radicals and preventing polymerization. EB curing stations must be properly shielded to protect the workers from ionizing radiation products [9].

Electron beams used in EB curing usually are generated in commercial applications in self-shielding EB curing equipment (Figure 2). Potentials in the range of 150,000 and 300,000 volts typically are used. 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 [7,18].

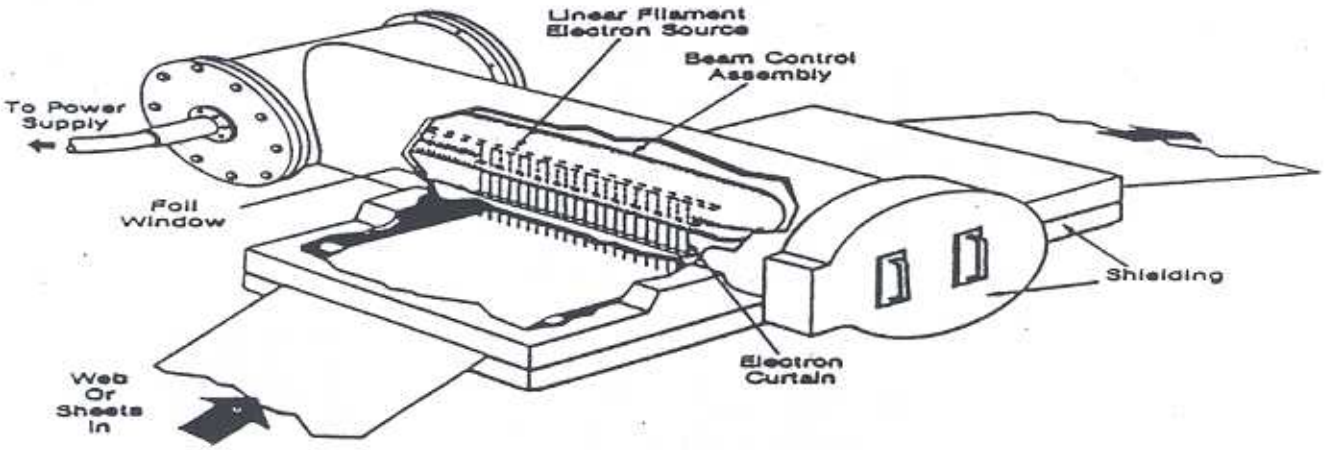

Figure 2. A linear filament electron beam printing installation

Coating Composition

EB-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 characteristic 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 its 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, the cure speed, the crosslink density, and the 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 [6].

Acrylates are the most commonly used monomers in current commercial systems, but a combination of as many as five monomers may be used 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.

Much formulation information is considered proprietary. However oligomers, monomers, and additives are weighed and mixed mechanically in batches and dispensed into containers for shipment to end users. Formulations usually are specific for each end user and determined by the required final film properties, the viscosity needed for the coating equipment, and the cure speed desired.

EB coatings can be formulated for almost any use as conventional coatings and applied by a number of methods classically used for the application of conventional coating systems, including roll coating, reverse roll coating, dipping, water curtains, spraying, and brushing. Due to the fast cure speed of these coatings systems, roll coating (or coil coating) is a popular coating method for radiation-curable coatings, as this method of application can be used to coat flat stock products at rates exceeding 1,000 ft/min [10]. Coating thickness typically is the minimum thickness necessary to obtain a continuous film, usually in the range of 0.2 to 0.5 mil [12]. EB curing of coatings on paper can be performed at a rate of 1,300 ft/min [9]. The faster line speeds with EB curing typically are used to increase production capacity, so that the extra capital equipment expense, relative to UV curing systems, can be justified. Faster line speeds with EB curing can be attributed to faster and more efficient polymerization processes.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Waste Generation

Roll coating of EB-curable materials is an extremely efficient process. Industry estimates of material waste generated using this method of application are conservatively less than 1% [10,14,16]. With radiation-curable materials, a conscious effort is made to maximize use efficiency because of the high cost of these materials. Overspray can be collected on baffles and reclaimed by filtering and viscosity restoration. Most of the waste generated will be in the form of residual materials left in the formulation supply containers, in the feed lines, and on the application rollers. Some waste may result from volatile compounds (monomer or additives), but contributions in this form may be considered negligible as a result of the low vapor pressure of the materials. Volatile emissions may become more significant in some situations where the rollers are heated to increase the flow properties of the coating. Essentially 100% conversion of the liquid coating formulation to hardened coating occurs during the EB curing stage, so no loss is assumed to occur here.

Most of the residual coating material can be cleaned from the roll coater using solvents, monomer, or water, and the resulting solution is fed into drums for proper disposal [13,17]. Cleaning generally is not a problem as the coatings remain in the liquid without exposure to the appropriate radiation source. Frequency of cleaning varies depending on the number of coatings being applied at a facility and the frequency of changeover. Facilities applying one coating only may be able to limit cleanup to twice yearly.

Accurately quoting industry-averaged data for the application of EB-curable formulations using roll-coating methods currently is not possible for several reasons:

- The diversity among the facilities applying radiation-curable coatings
- The infancy of the radiation-curable industry
- The proprietary nature of the industry.

An audit of five facilities that roll coat radiation-curable formulations demonstrated use rates of 5,000 to 50,000 gallons of coatings per year [13]. Although the number of workers per site varies significantly, the following worker breakdown may be appropriate when considering worker exposures during roll coating processes [13]:

- 1 worker responsible for handling raw materials, 1 shift per day, primary risk of exposure to coatings
- 2 workers to maintain a given roll-coating line, average of 2 shifts per day, greatest risk of exposure to coating formulations
- 1 worker for quality assurance, 1 shift per day, primarily exposed to formulations when testing materials delivered to site
- 1 worker for maintenance, 1 shift per day, periodic exposure.

Although some of the constituents of the radiation-curable materials may be considered unfriendly, the formulation of these materials appears to be a relatively safe practice. This is due primarily to the fact that most of the materials are transferred using pumps and feed lines, and to the low vapor pressure of the radiation-curable formulations [13]. In addition, due to the nature of some of the components, safe worker practices, proper clothing, and engineering controls usually are strictly enforced. Elephant trunks, hooked into local exhaust ventilation systems, typically are used to supply ventilation at the emission points. The acrylic monomers used in the formulations usually are considered to pose the most threat to the workers. The Occupational Safety and Health Act (OSHA) currently defines the time-weighted average (TWA) legal allowable air concentration to be 25 ppm for ethyl acrylate, 10 ppm for methyl acrylate, and 100 ppm for methyl methacrylate [13].

the following

Information available on facilities applying radiation-curable coatings by roll coating is not well established. As such, assumptions will have to be made to allow environmental releases and worker exposure-level calculations to be made. Basic ~~assumptions for the following calculations are as follows:~~

- 454 grams of dried (cured) coating to coat 1,000 ft^2 of substrate [20]
- 100% of the radiation-curable coatings converted to dry product; therefore 454 grams of wet radiation-curable coating to coat 1,000 ft^2 of substrate
- roll-coating application on only one face of the substrate
- web width of 6 feet
- line speed of 300 ft/min.

Based on these assumptions, coatings will be used at a rate of 820 g/min or 49 kg/hr.

Variables/Assumptions

F PMN - PMN: weight percent of PMN material, given by manufacturer or estimate as 5% additive, 60% monomer, 35% oligomer.
Note - NS: number of sites applying coating with PMN material, given by manufacturer
N roll coaters - RC: number of roll coaters in operation per site, assumed to be 1
T shift - H: 8-hour shifts
N shift - Sh: 2 shifts per day
T production - DOP: 250 days of production per year
Eff operating - Eff: operating efficiency of site; assume 70%
RATE breathing - IR: worker breathing rate (m^3/hr)
C respirable constituent - CR: concentration of respirable constituents in the air (mg/m^3)
VP - P: vapor pressure of the PMN at room temperature (mmHg)
MW - MW: molecular weight of the PMN material
N transfer - TR: number of transfer operations per day involving PMN material

Use Rate of Coatings (kg/site year)

Generic: PMN x 49 kg/h × RC × H × Sh × Eff × DOP = ??(kg/site yr)

PMN × 49 kg/h × 1 roll × 8 h × 2 shifts × 70% = PMN × (550) kg/site day

PMN × 49 kg/h × 1 × 8 h × 2 shifts × 70% × 250 day/yr = PMN × (1.4×10^5) kg/site yr

Environmental Releases (kg/site day)

Radiation-curable coatings remain in liquid form until exposed to the proper form of radiation, at which time polymerization and crosslinking form a cured film. Roll coating is claimed to be a 99+% efficient process, i.e., almost all of the coating materials dispensed end up as cured product on the part. Therefore, at most, 1% waste is created in the liquid form. In some instances, EB formulations remaining in packaging materials and drums are cured (solidified) in the container to allow for disposal of the containers as nonhazardous waste. Solid coating waste in this form is considered negligible and indistinguishable from the container. As such, the only waste of interest is the waste generated and remaining in the liquid form. Although some spillage is expected, this waste is generated primarily in diluted forms during equipment cleaning.

Liquid Waste: Liquid waste from cleaning and spills is stored in drums for disposal as hazardous waste.

Generic: PMN × 49 kg/h × RC × H × Sh × Eff × 0.01 = ??(kg/site yr)

PMN × 49 kg/h × 1 roll × 8 h × 2 shifts × 0.7 × 0.01 = PMN × (5.5) kg/site day

Water Emissions: In the worst case, liquid waste could become a water emission.

Solid Waste: None assumed.

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)

Exposure hazards for radiation-curable coatings are limited to liquid exposures. 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 is in the form of liquid vapor formed during application. An inhalation rate of 1.25 m^3/hr is assumed [21]. If the concentration of the liquid or vapor phase in the air is not known, the permissible exposure limit (PEL) for the formulated coating may be assumed.

Generic: PMN × CR × IR × H = ??(mg/day)

Roll coating of radiation-curable coatings involves the transfer of coating formulations from the shipping containers to the pickup troughs. This operation poses a periodic threat to the workers performing this task. Inhalation of liquids depends on the volatility of the liquid agent (assumed to be the PMN). Most of the components of radiation-curable coatings have very low vapor pressures and are considered nonvolatile liquids. If this is not the case for the PMN material, the following consideration should be made to estimate the concentration of the PMN in the air during transfer of the PMN material from a 55-gal drum to the mixing vessel [21]. This is a worst-case approximation, assuming open-system manual feeding.

$$CR_{trans}\ (PMN)\ (mg/m^3) = (95 \times P) \times (MW/24.5\ L/mole)$$

Then, inhalation exposure during the transfer of liquid PMN material can be determined as:

$$CR_{trans}(PMN) \times IR\ (1.25\ m^3/h) \times \text{transfer per day} = \underline{??(mg/day)}$$

Dermal Exposure: Dermal exposure is limited to incidental exposure from materials handling during transfer. This includes handling liquid coating formulations and consequent exposure to the PMN material during any transfer operations involving the coatings formulations. One contact results in exposure for the entire day. Equations approximating exposure levels are based on data compiled on contact operations as given in CEB (1991, Table 4-13) [21].

$$\text{Liquid Dermal Exposure: } (1300\text{ -}3900)\ mg/m^3 \times PMN/100 = \underline{??(mg/day)}$$

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