Generic Scenario: Roll Coating of UV-Curable Coatings

Introduction

Roll coating is a coating application method very similar to printing in that an elastomer-covered steel roller is used to transfer a coating to a flat substrate moving past the roller [11]. It is very efficient as it 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 feet per minute (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. However, the use of UV-curable coatings in roll or coil coating of metals is limited by the inability of the UV radiation to penetrate and cure thick or highly pigmented coatings.

Market

Much of the market information on radiation-curable materials does not differentiate according to the formulated product (e.g., coating, ink, adhesive) and little market share information is reported based on the application method of UV coatings [11]. Some market share information can be inferred from other market information.

The UV-curable market was approximated as comprising 90% of the total radiation-curable market, or about 46 million pounds in 1990 [2,5]. 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]. Based on dollar value, coatings accounted for 44% of the 1991 market for radiation-curable materials; inks, 16%; electronics, 32%; adhesives, 4%; and other end uses, 4%, as seen in Table 1 [3].

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

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

The radiation-curable coatings market as a whole 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 UV-curable 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 maintain extremely high production rates for coating flat stock products. UV clearcoats on paper may be run as fast as 1,000 ft/min in properly configured systems [10]. Although not all roll or coil coatings use UV-curable coatings, 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 per 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.

Among the UV coatings, 38% are estimated to be applied to plastic substrates, 34% to wood, 22% to paper, and 6% to metal [7]. UV-curable coatings are used for plastics, metals, wires, textiles, glass, wood, paper, no-wax vinyl flooring, fiberglass laminates, photoresists, printing plates, fiber optics, release coatings, magnetic tape, and compact disks, and as conformational coatings for electronics applications [3,6]. One of the first applications for UV-curable coatings was for furniture and filler boards. No-wax flooring was made possible by UV-curable clearcoats on heat-sensitive vinyl sheets [6].

Technology Description

Roll coating is very similar to printing in that an elastomeric-covered steel roller is used to transfer the coating to a flat substrate moving past the roller [11]. This very efficient process is capable of applying a thin, well-controlled coat of paint at very high speeds [11]. 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].

Roll-coating methods for UV-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 are usually 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 is a flow diagram for a roll-coating line.

Once the UV-curable materials are applied, the coated product material is transported to the UV staging area for curing. UV-curable coatings are activated by a chemical process that uses ultraviolet radiation to polymerize and crosslink the polymeric coatings. Light energy is absorbed by a photoinitiator that generates highly reactive free-radical or cationic species. Most current industrial applications use free-radical photopolymerization to initiate the polymerization of the functionalized oligomers and monomers into highly crosslinked, chemically resistant films [6].

Cure is rapid, on the order of a few seconds, but is limited to line-of-sight curing. Production rates attainable with UV-curable materials are somewhat slower than the 1,000 ft/min attainable with EB-curable materials. A 400-watt/inch UV lamp can cure clear UV formulations on plastic at a rate of 300 ft/min, metal at 200 ft/min, and wood at a rate of 25 ft/min [9]. A medium-pressure mercury lamp is the most common source of UV radiation. Only the coating directly impinged by the UV radiation will be cured. Roll or web products are ideal configurations for

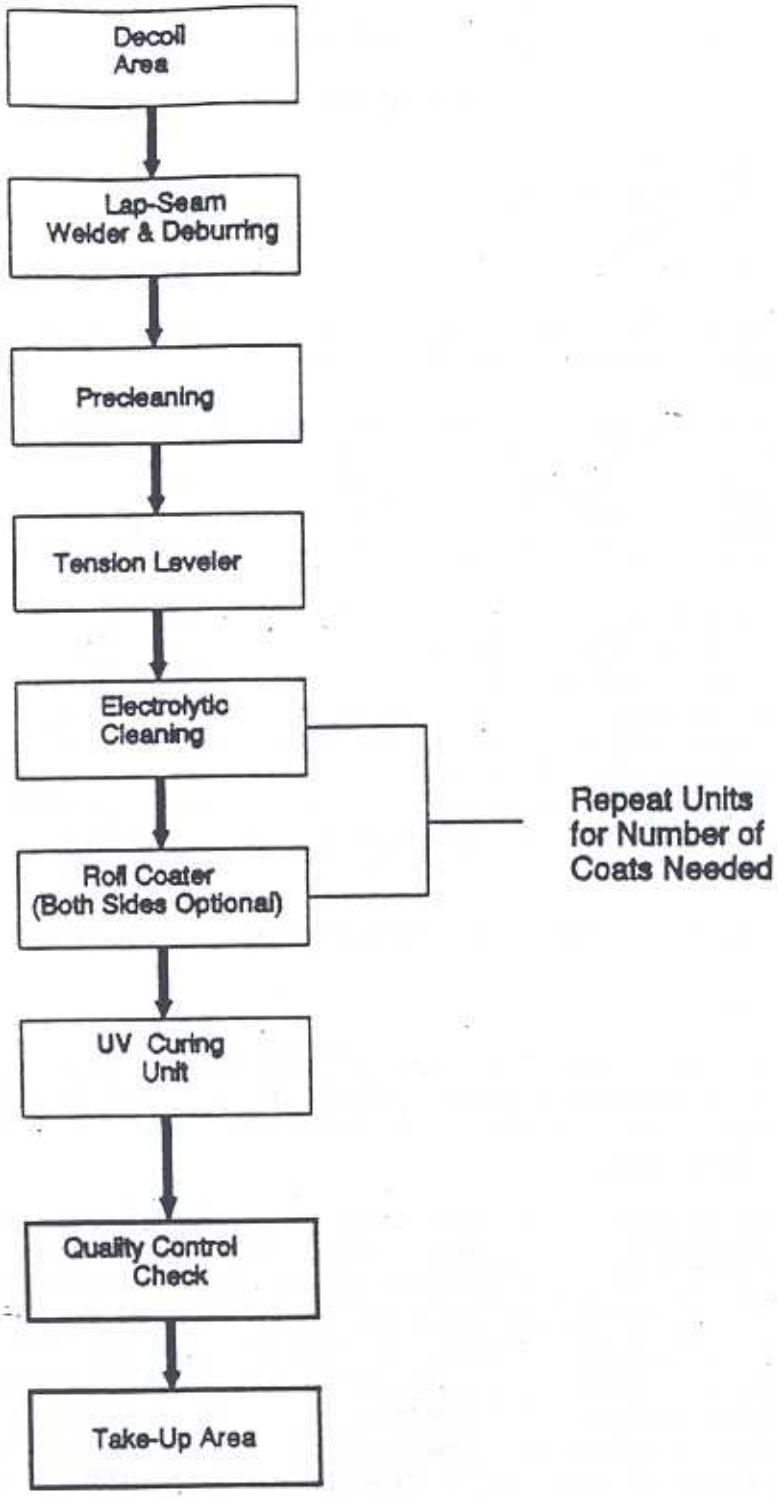

Figure 1. Flow Diagram of Roll-Coating Line for UV-Curable Coatings

UV curing, but intricate product shapes are difficult to cure by UV. Except in certain electronic applications where high purity is essential, UV curing can be performed in the presence of air [10]. The rate of the reaction is affected by the light intensity, selection of photoinitiator, and selection and concentration of reactive monomers.

UV-curable coating formulations have four basic components:

- photoinitiator (1 to 3%)
- oligomers (25 to 90%)
- monomers (15 to 60%)
- additives (1 to 50%) [6].

Photoinitiators are the link between the light source and the oligomers and monomers [6]. The photoinitiator absorbs UV energy and produces free radicals or cations.

Oligomers provide the cured coating with its characteristic physical properties [6]. Oligomers usually are functionalized for UV-curable coatings by reacting with an acrylate such as hydroxy ethyl acrylate or hydroxy propyl acrylate. The functionalized oligomers used most commonly are acrylated epoxy, acrylated urethane, acrylated polyether, and acrylated polyester [6]. Other oligomers, including vinyl ether-functionalized urethanes, epoxy-silicone, and epoxy-siloxane oligomers, may be used to obtain very specific final film properties [17].

Monomers are important in determining the coating viscosity, the cure speed, the crosslink density, and the final surface properties of the film [6]. As many as five monomers may be used in a single formulation to balance cure speed and final properties. Acrylates are the most commonly used monomers in current commercial systems. Other monomer systems include styrene, N-vinyl pyrrolidone, and vinyl ether [18,19]. Additives for UV systems include pigments, dispersants, stabilizers, etc., typically used in conventional coating systems. Formulations may include up to 50% additives to yield the desired the final film properties [6]. These cannot interfere with the curing process. Pigments typically absorb and scatter UV radiation, so most UV-curable coatings are essentially clear, having pigment levels of the order of 4 to 5% by weight, and less than 10% by weight total additives [10].

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Waste Generation

Roll coating UV-curable materials is an extremely efficient process. UV-curable coatings are 100% reactive. 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.

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 UV 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 [10,13]. Cleaning generally is not a problem as the coatings remain in liquid state until exposure to UV. Packaging containers in which the coating materials are supplied are subjected to UV radiation to cure the residual materials to an inert state for disposal. Frequency of cleaning varies, depending on the number of coatings being applied at a facility and the frequency of changeover.

Worker Exposure

Care must be taken to ensure that workers are protected from harmful exposure to UV radiation during curing by shielding the UV source. Figure 2 shows a mercury vapor UV curing unit.

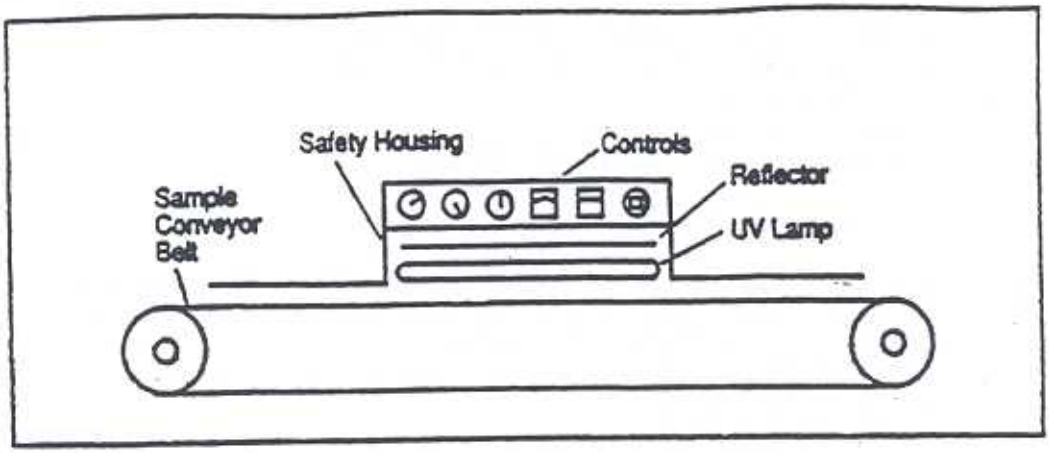

Figure 2. Typical Mercury Vapor Ultraviolet Radiation Curing System [4]

Although some of the constituents of radiation-curable materials may be considered unfriendly, roll coating appears to be a relatively safe practice for these materials. This is due primarily to (1) the fact that most of the materials are transferred using pumps and feed lines, and (2) the low vapor pressure of the UV-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 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].

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

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

An audit of five facilities that roll coat radiation-curable formulations demonstrated use rates ranging from 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.

Quantitative information on facilities applying radiation-curable coatings by roll coating is not well established. Assumptions will be made to allow environmental releases and worker exposure-level calculations for a model facility running two 8-hour shifts per day for 250 production days per year at one site:

- 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
- application by roll coating only on one face of the substrate
- web width of 6 feet
- line speed of 300 ft/min
- coating used at a rate of 820 g/min or 49 kg/hr.

454 g coating / ft^2 substrate

Definitions of Terms/Variables Needed for Exposure Calculations

F_{PMN} - PMN: weight percent of PMN material given by manufacturer or estimated by type of component in UV-curable coating formulation and coating volume used by manufacturer per site per unit of time (e.g., photoinitiator PMN could be 1 to 3%)

N_{sites} - NS: number of sites applying coating with PMN material, given by manufacturer or estimated from production volumes

$N_{roll-coaters}$ - RC: number of roll coaters in operation per site, given by manufacturer or estimated from production volumes

T_{shift} - H: length of shifts, usually 8 hours in the USA

N_{shift} - Sh: number of shifts per day; usually 1 to 3 in the USA depending on shift length (H)

$T_{production}$ - DOP: days of production per year, usually estimated at 250 days per year in the USA.

$Eff_{operating}$ - Eff: operating efficiency of site; assume 70%

$Rate_{breathing}$ - IR: worker breathing rate (1.25 m^3/hr)

$Conc_{cont}$ - CR: concentration of respirable constituents in the air (mg/m^3); vapor pressure from literature or from manufacturer is required

VP - P: vapor pressure of the PMN at room temperature (mmHg); dependent on the individual PMN

MW - MW: molecular weight of the PMN material; available by calculation [21]

$N_{transfer}$ - TR: number of transfer operations per day involving PMN material; estimate based on number of shifts, use rate of coatings, and equipment size

These variables should be estimated individually for each facility studied.

Use Rate of Coatings (kg/site year)

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

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

PMN × 550 kg/site day × 250 day/year = PMN × (1.4×10^5) kg/site year

Environmental Releases (kg/site day)

UV-curable coatings remain in liquid form until exposed to UV radiation, at which time polymerization and crosslinking forms a cured film. Roll coating is claimed to be a 99+% efficient process in terms of materials, 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.

Liquid Waste: Although some spillage may be expected, liquid waste is generated primarily in diluted form during equipment cleaning. This liquid waste collected in drums is disposed of as hazardous waste by government-approved methods.

Generic: PMN × 49 kg/h × RC × H × Sh × Eff × percent waste = ??(kg/site year)

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

Solid Waste: In some instances, UV 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 is indistinguishable from the container.

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

Water Emissions: In a worst case, liquid used for cleaning or other purposes could be released to water. The amount of PMN released would be that calculated above under liquid waste.

Worker Exposure (mg/day)

Exposure hazards for radiation-curable coatings are limited to liquid exposures. The method of transfer of UV-curable materials from shipping containers to mixing and applying equipment depends on the usage volume, size of containers, and size and type of coating reservoirs and application equipment. Exposure levels are determined for 1 worker working one 8-hour shift and making one transfer in a given day at the model facility.

Inhalation Exposure: Exhaust and ventilation systems prevent the buildup of ozone in the curing area. The in-plant inhalation threat is in the form of liquid vapor formed during application or transfer of coating formulations from the shipping containers to the pickup troughs. Application lines are extensively shielded and vented to minimize the exposure to line workers. Transfer poses a periodic threat to the workers performing this task, especially if materials are added by hand. Inhalation of vapor or mist will depend on the volatility of the liquid agent (assumed to be the PMN). Vapor pressure information for many chemicals is available in the scientific literature or may be calculated [21]. 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. An inhalation rate of 1.25 m^3/hr will be assumed.

Inhalation during shift:

defined 8 hrs/shift

2 shifts/day

∴ 16 hrs/day

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

example Model: PMN × CR × 1.25 m^3/hr × 8 = ??(mg/day)

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

Generic: CR_{trans}(PMN) × IR × TR (transfers per day) × H (hr per transfer) = ??(mg/day)

example Model: CR_{trans}(PMN) × (1.25 m^3/h) × 1 transfer per day × 8 hr per transfer = ??(mg/day)

Inhalation exposure due to mist: Total mist concentrations (8-hr TWA) for inhalation exposure estimations for workers are recommended for cases involoving roll coating of UV-curable inks and coatings:

0.04 to 0.26 mg/m^3

$\frac{\text{shifts}}{\text{day}} \left(\frac{\text{1 transfer}}{\text{shift}}\right)$

implies ½ transfer per shift (other scenario assume 2 shifts/day)

This data is from a submitted PMN case and is intended only to give CEB a basis for estimations when no other data are available. There are many uncertainties associated with these data and their use. The following are some of the background information on and the caveats to these data. There are 10 data points total, including 3 personal monitoring and 7 area data points (see Table 2). The range of 0.04 to 0.26 mg/m^3 includes only data for the personal samples. Personal monitors were positioned in the operators' breathing zones, and area monitors were positioned at head height in the operators' area close to the print rollers. Collection media from monitors were solvent extracted, and the soluble fraction were assumed to be "ink fly" or ink misting as the ink film splits in transferring from roller to roller. The operation monitored was in a facility using offset lithographic printing of cartonboard for retail food packaging; the facility location may have been in the United Kingdom. Representativeness of these data relative to actual ink fly concentrations in the universe of similar operations is unknown; however, it seems reasonable that this data could be applied to other similar operations.

Table 2
Monitoring Data for Ink Fly Mist of UV-Curable Coating used in Offset Lithography

Sample	Sample Type	Sample Volume (L)
1	personal	170
2	personal	200
3	personal	144
4	area	291
5	area	360
6	area	357
7	area	546
8	area	306
9	area	306
10	area	189

Table 2 notes:
-Operation is printing of cartonboard for retail food pacaging.
-Data is submitted for PMN case.
-Amount trapped is solvent extracted (soluble) fractionof total airborne particulate.
-Exposure concentration (mg/m^3) = (amount trapped (µg)/sample volume (L))*1000 L/m^3/1000 µg/mg

Dermal Exposure: Dermal exposure is limited to incidental exposure from materials handling during transfers. This includes handling liquid coating formulations, and consequent exposure to the PMN material during any transfer operations involving the coatings formulations. TR represents the frequency with which these transfer operations take place per day. Equations approximating exposure levels are based on data compiled on contact operations as given in CEB (1991, Table 4-13) [21].

Liquid Dermal Exposure

Generic: (1,300 - 3,900) mg/day × TR × PMN/100 = ??(mg/day)

Model: 3,900 mg/day × 1 transfer per day × PMN/100 = 390 PMN mg/day

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