Generic Scenario: Formulation of UV-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, UV-curable systems cannot accommodate high pigment loadings. The UV radiation must penetrate the coating to cure.

UV-curable coatings typically are used for plastic, metal, wire, textiles, glass, wood, paper, no-wax vinyl flooring, fiberglass laminates, photoresists, printing plates, fiber optics, release coatings, magnetic tape, compact disks, and 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]. Of the radiation-curable coatings, 38% are estimated to be applied to plastic substrates, 34% to wood, 22% to paper, and 6% to metal [7].

Market

Much of the information on radiation-curable materials does not differentiate according to the formulated product (e.g., coating, ink, adhesive), but instead 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 because 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 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 the United States [3]

End Use	1991 Market Share (%) Based On Dollar Value
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 UV-curable market may be approximated as comprising 90% of the total radiation-curable market. This could be as much as 45.9 million pounds of UV-curable coatings produced in the United States in 1990.

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 several 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 needed
- little or no solvent content, thus minimizing or eliminating volatile organic compound (VOC) emissions during coating operations
- elimination of the high costs associated with the handling and disposal of the solvents, or solvent abatement systems.

UV Technology Description

UV curing is a chemical process that uses ultraviolet radiation to polymerize and crosslink the polymeric coatings. Light energy is absorbed by a photoinitiator, which generates highly reactive free-radical or cationic species. Most current industrial applications use the free-radical type photopolymerization process [6]. These reactive species initiate the polymerization of the functionalized oligomers and monomers into highly crosslinked, chemically resistant films. Cure is rapid, on the order of a few seconds. The rate of the reaction can be affected by the light intensity, selection of photoinitiator, and selection and concentration of reactive monomers. A medium-pressure mercury lamp is the most common source of UV radiation. The intensity of the UV output from these lamps, typically about 200 watts/inch, enables line speeds of several hundred feet per second to be utilized efficiently, depending on the geometry of the part and the specific UV-curable formulation [6].

UV Coating Formulation

UV-curable coating formulations have four basic components:

- photoinitiator (1 to 3%)
- oligomers (25 to 90%)
- monomers (15 to 60%)
- additives (1 to 10%) [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. The two types of free-radical photoinitiators most commonly used are the abstraction type (e.g., benzophenone, xanthones, and quinones) and the cleavage type (e.g., benzoin ethers, acetophenones, benzoyl oximes, and acylphosphines). Cationic photoinitiators are arylsulfonium salts that decompose when exposed to UV light to produce positive ions. Bronsted acids such as iodonium, sulfonium, and selenonium are common for cationic systems [4,6]. The coating will not cure unless exposed to UV radiation.

Oligomers provide the cured coating with its basic 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]. Each imparts a different set of physical properties to the final coating. Other oligomers, including vinyl ether-functionalized urethanes, epoxy-silicone, and epoxy-siloxane oligomers, may be used to obtain very specific final film properties [8].

Monomers are important in determining the coating viscosity, cure speed, crosslink density, and 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 [9,10].

Additives for UV systems include pigments, dispersants, stabilizers, etc., typically used in conventional coating systems. Formulations may include up to 50% additives to yield desired final film properties [6]. These cannot interfere with the curing process. Pigments typically absorb and scatter UV light, so highly pigmented

coatings/inks generally require EB curing. Most UV-curable coatings are essentially clear, having pigment levels on the order of 4 to 5% by weight and less than 10% by weight total additives [11].

Manufacturing Process

The process for manufacturing UV-curable coatings essentially consists of blending the raw materials comprising the formulation into a precisely ratioed and homogeneously blended product [11,12]. Figure 1 illustrates simple batch process equipment. 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 [12]. 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]. The formulation of radiation-curable coatings is a specialty market, so the batch sizes used during manufacture vary greatly from several gallons to thousands of gallons [11,12]. The raw materials sometimes are preheated (110 to 150°F) to lower the viscosity of the components to facilitate transfer [13], thus increasing the vapor pressure of the raw materials.

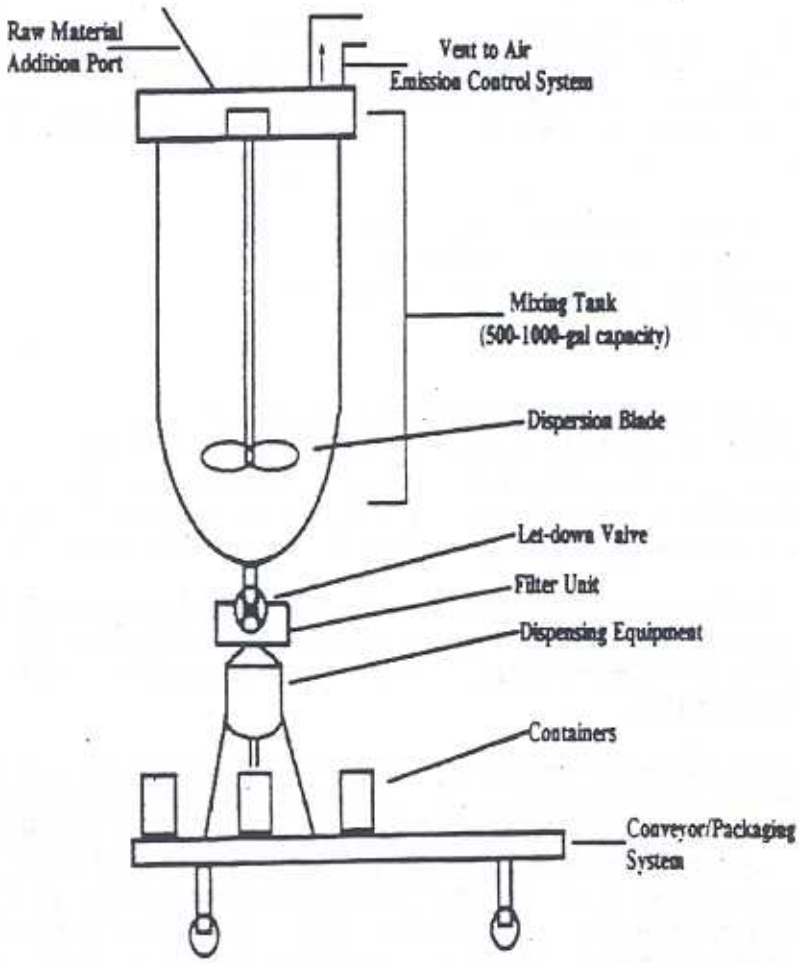

Figure 1. Schematic of UV-Curable Coating Formulation Equipment

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 liquid form and can be fed into the mixing kettle using pumps and feeds tubes [12].

Once mixing is completed, quality assurance samples typically are drawn from the kettle for assessment [11,12]. 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 [11]. 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 [11,12]. However smaller containers are not uncommon, including 1 and 5 gal buckets, or even syringes [11].

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]. It is so high primarily because of 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 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. This industry has a strong industry association that controls information about the formulation and application of radiation-curable coatings. Currently, there are more than 100 formulators of radiation-curable coatings in the USA [12]. Information about the production capacity of these facilities and 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 constituents of 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 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 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. OSHA currently defines the legal allowable air concentration in time-weighted average (TWA) to be 25 ppm for ethyl acrylate, 10 ppm for methyl acrylate, and 100 ppm for methyl methacrylate [13].

Variables/Assumptions

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 are now formulating some quantity of UV-curable coatings and could quickly 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. Some assumptions will be presented when appropriate. A 1,000-kg basis is used for example calculations. Most calculations are done on a per site basis.

$F_{(PMN)}$	- PMN:	weight percent 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%.
Size batch	- BS:	average batch size (kg); assume 1,000-kg basis
N batch	- NB:	number of batches produced per shift; assume 2
N site	- NS:	number of sites using PMN material; could be from 1 to 100
T shift	- H:	8-hour shifts
N shift	- Sh:	2 shifts per day
T production	- DOP:	250 days of production per year
RATE breathing	IR:	worker breathing rate (1.25 m^3/h)
Concentration - workplace	CR:	concentration of respirable constituents in the air (mg/m^3)
VP	- P:	vapor pressure of the PMN at room temperature (mmHg)
MWt	- MW:	molecular weight of the PMN material
N transfer	- TR:	number of transfer operations per day involving PMN material; for calculations assume that one transfer results in exposure for the entire day

Production of UV Formulations (kg/site year)

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

PMN × 1,000 kg × 2 batches × 2 shifts = PMN × (4,000 kg/site day)

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

If volume of PMN produced is desired, divide the weight produced by the density of the PMN.

If production of PMN is desired assuming use by all U.S. producers, multiply the percent PMN by the 1990 annual production of UV-curable coatings, or 45.9 million pounds (2.1×10^7 kg).

Environmental Releases (kg/site day)

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

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

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

Liquid Waste: 1% of product may be 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: $PMN \times BS \times NB \times Sh \times 0.01 =$??(kg/site day)

$PMN \times 1{,}000$ kg $\times$ 2 batches $\times$ 2 shifts $\times 0.01 = PMN \times (40)$ 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 will be provided for both solid and liquid PMN materials. Most UV-curable coatings have little or no pigment. Exposure levels will be determined for 1 worker working one 8-hour shift in a given day.

Inhalation Exposure:

(i) 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 [13].

Generic: $PMN \times CR \times IR \times H =$??(mg/day)

(II) 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 [13]. This is a worst-case approximation, assuming 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 Thus, inhalation exposure during the transfer of liquid PMN material can be determined as:

$$CR(PMN) \times 1.25\ m^3/h \times 1 \text{ transfer per day} \times 8 \text{ hours per day} = \underline{??(mg/day)}$$

(iii) Sometimes the PMN materials are supplied as a powder, which will pose an inhalation threat when being 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:

$$15\ mg/m^3 \times 1.25\ m^3/h \times 1 \text{ transfer per day} \times 8 \text{ (hours exposure per transfer)} = \underline{??(mg/day)}$$

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 on compiled on contact operations as given in CEB, Table 4-13 [13].

Liquids: $(1{,}300 - 3{,}900)\ mg/m^3 \times TR \times PMN/100 = \underline{??(mg/day)}$

Solids: $(6{,}500 - 18{,}200)\ mg/m^3 \times TR \times PMN/100 = \underline{??(mg/day)}$

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MEMO

SUBJECT: Update of Generic Scenario for UV-curable Coatings

Date: September 19, 1995

From: Scott

To: CEB

Summary

The current generic scenario (no date) assumes no inhalation exposure due to mist generated by the roll coating process. However, recently submitted data (see Table 1, attached) from a PMN case indicates that such exposure can occur. Based on that data, the following total mist concentrations (8-hr TWA) for inhalation exposure estimations for workers are recommended for cases involving roll coating of UV-curable inks and coatings:

0.04 to 0.26 mg/m^3 (what-if).

You may want to attach this memo to your current copy of the generic scenario.

Background

As with many of CEB's generic scenarios, this memo 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 caveats to these data. There are 10 data points total, including 3 personal monitoring and 7 area data points. The range of 0.04 to 0.26 mg/m^3 includes only data for the personal samples, which are assumed to be representative of 8-hr TWA. It may be noted that data from area samples are similar to data from 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.

(over)

Table 1
Monitoring Data for Ink Fly Mist of UV-Curable Coating used in Offset Lithography

SAMPLE	SAMPLE TYPE	SAMPLE VOLUME (litres)	AMOUNT TRAPPED (ug)	EXPOSURE CONCENTRATION (mg/m^3)
1	Personal	170	44	0.26
2	Personal	200	12	0.06
3	Personal	144	5	0.04
4	Area	291	8	0.03
5	Area	360	17	0.05
6	Area	357	22	0.06
7	Area	546	12	0.02
8	Area	306	14	0.05
9	Area	306	8	0.03
10	Area	189	ND	NA

Table 1 Notes:

Operation is printing of cartonboard for retail food packaging.

Data is submitted for PMN case.

Amount trapped is solvent extracted (soluble) fraction of total airborne particulate..

ug = micrograms; ND = none detected; NA = not available.

Exposure concentration (mg/m^3) =
amount trapped (ug) / sample volume (L) * 1000 L/m^3 / 1000 ug/mg