GENERIC SCENARIOS FOR INITIAL ENGINEERING REVIEWS

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MANUFACTURE AND USE OF PRINTING INK

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Prepared for the Chemical Engineering Branch by SAIC

Introduction

The printing industry is a large, geographically diverse industry sector which employs over 810,000 workers nationwide (PIA, 1993). Four basic processes are used in the industry: screen printing, letterpress, gravure, and lithography. Screen printing transfers the ink to the substrate through a screen marked with a stencil. It is used for short print runs of artistic images, especially on objects that cannot be printed by other means. Letterpress, the oldest printing process, uses a raised metal image on a printing cylinder. It is difficult to print high-quality shaded images by this process, and it has largely fallen out of favor. Gravure relies on an image etched into a printing plate. It gives very sharp line quality and was formerly used for maps; it is still used for currency. The dominant printing process, however, is offset lithography, which accounted for 85% of printing in 1993 (PIA, 1994). This uses a flat printing plate that has been photochemically treated to absorb an oil-based ink in the image areas and to absorb only water in the non-image areas. This generic scenario will focus on the manufacture and use of lithographic inks.

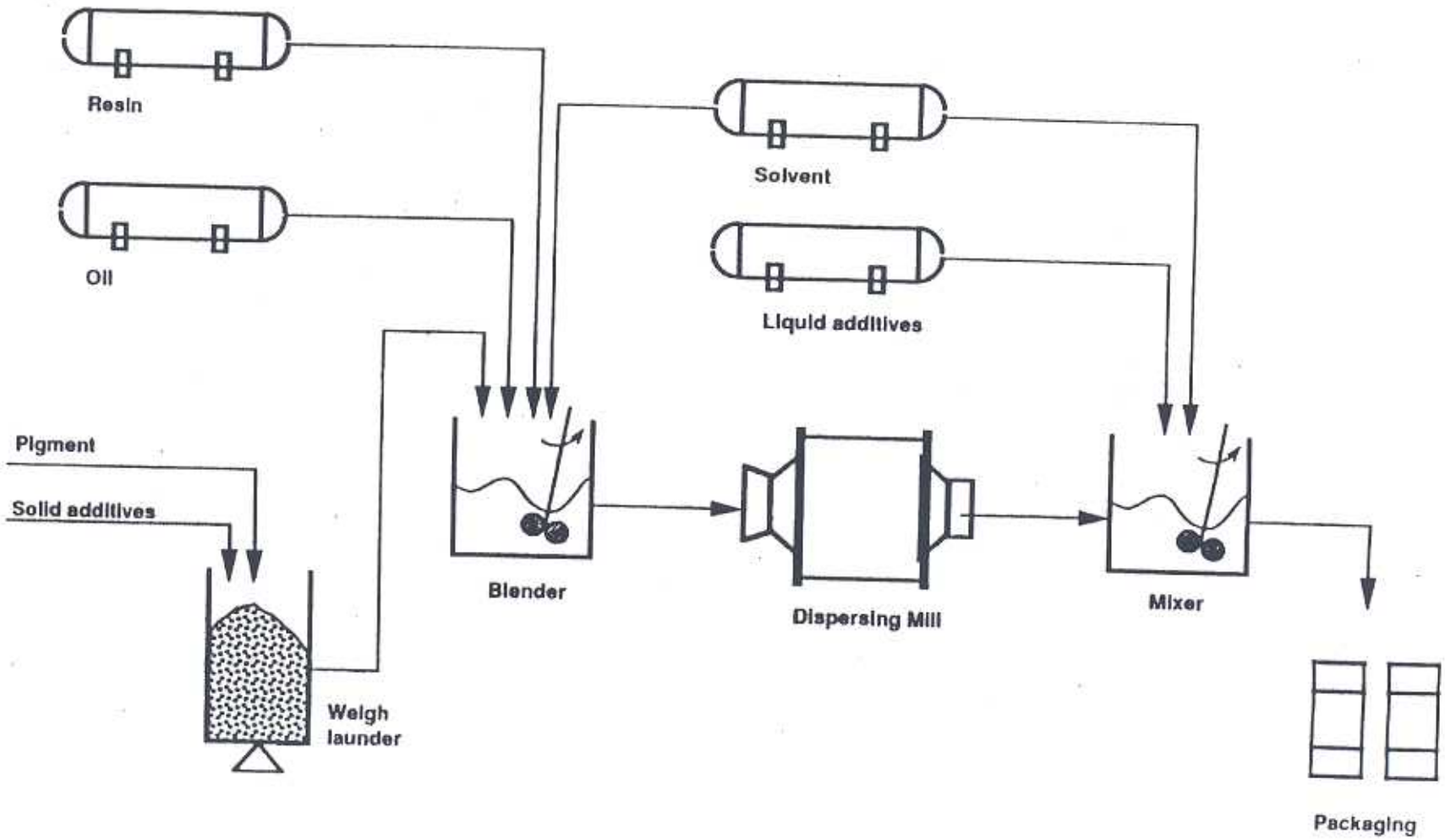
In some cases, the PMN submitter may be an ink manufacturer and the manufacturing process may be fully described in the PMN. More frequently, however, the PMN submitter is a manufacturer of resins, pigments, solvents, or other components which are sold to ink formulators. For this reason, the ink manufacturing process is described in some detail in this generic scenario.

MANUFACTURE

Process Description

Ink manufacture resembles paint production in many respects. Figure 1 illustrates the main features of the process. A vehicle consisting of resin, solvent, drying agents, and resin plasticizing oils is prepared. Pigment is blended into the vehicle and the mixture is fed to a dispersing mill. The milling step may be dispensed with if the pigment is already finely ground and the blending process is sufficient to produce a uniform product. The raw ink is then let down with additional solvent and other additives and packaged for sale. Lithographic and letterpress inks are sold as viscous pastes. Other inks contain a higher proportion of volatile solvents and are more liquid.

Process Flow Diagram for the Manufacture of Printing Inks



Number of Manufacturing Sites

According to Department of Commerce statistics, there are 150 lithographic ink manufacturing plants in the United States (DoC 1993). In 1992, 135 ink plants, not necessarily all lithographic ink producers, reported to the Toxics Release Inventory (SIC code 2893). These ink formulators produced about 275 million kilograms of lithographic ink in 1992.

To compute the number of sites, first estimate the amount of ink that can be produced using the PMN. Assume that ink contains 30-35% solvent, 10-35% resin (the lower number is for newspapers, the higher one for glossy brochures), 15-20% pigment, and 5-25% vegetable oil (NAPIM, 1994). Then use:

$$NS = \frac{(PV \times 100)(150)}{(PPI)(275 \times 10^6)}$$

where

NS	=	Number of sites
PV	=	Production volume of PMN chemical, $kg.yr^{-1}$
PPI	=	Percent PMN chemical in ink

Average employment at ink formulation plants was 30 employees in 1992 (DoL, 1992). Assume that 10-15 of these workers may have direct contact with the ink, the remainder being engaged in management, warehousing, and other functions.

Worker Exposure

A. Inhalation

Most recent PMN submissions have been for non-volatile components of the ink, usually the resin or the pigment. However, if the PMN chemical is volatile, it will be necessary to estimate inhalation exposures. NIOSH conducted a relatively detailed sampling program at Consolidated Printing Inks in West St Paul, Minnesota. If the 109 data points from this sampling event are analyzed, it is possible to arrive at the following model for solvent exposures during printing ink manufacture:

$$C_m = 0.074 M P x_i$$

where

M	=	Molecular weight of chemical i
x_i	=	Mole fraction of i in the solvent mixture
P	=	Vapor pressure of i
C_m	=	Airborne concentration of i, $mg.m^{-3}$

The derivation of this equation is given in Appendix A. For particulate exposures, assume that the total particulate concentration in the air is 2 $mg.m^{-3}$. This was the average value found at the Consolidated Printing Inks site.

B. Dermal

Use standard CEB assumptions.

Environmental Releases

A. Air

The 135 ink formulating plants that reported to the 1992 Toxics Release Inventory reported an average air release of 26 $kg.day^{-1}$ of VOCs. The rate of release of the PMN chemical should therefore be:

$$Q_i = 26 \frac{x_p P_p M_p}{\Sigma x_i P_i M_i}$$

where

Q_i	=	Mass flux of PMN chemical, $kg.site.^{-1}day^{-1}$
x_i	=	Mole fraction of chemical in solvent mixture
x_p	=	Mole fraction of PMN chemical in solvent mixture
M_i	=	Molecular weight of chemical
M_p	=	Molecular weight of PMN chemical
P_i	=	Vapor pressure of chemical
P_p	=	Vapor pressure of PMN chemical

B. Water

No releases to water are expected from ink manufacturing plants. The Toxics Release Inventory and other Federal databases show zero or low water releases from this SIC code.

C. Landfill/Incineration

Releases of solid waste will consist of container residue (1-4 % of PMN volume) and equipment cleanout (0.2-2%).

$$\frac{(1.2 - 6\%) \times PV}{4 \text{ sites} \times 24}$$

USE

Process Description

At the printing facility, the PMN-containing ink paste is unloaded from a container into an ink tank on the printing machine. The machine is set in motion and ink is transferred first to the ink rollers, then to the printing cylinder, then to the offset blanket, and finally to the paper. A typical small printshop has a single 2-color sheet-fed press, usually with a nominal plate area of 11 x 17". A larger plant will have one or more 4-color or 6-color presses with a nominal plate area of 28 x 40" (UofTenn, 1994). The larger presses may be sheet-fed or web-fed. At the end of the working day, or when the plates are changed, the press is cleaned. This is generally done by using a squirt bottle to pour a steady stream of solvent onto the first set of cylinders while the machine is set to recycle sheets of absorbent paper back and forth through the press. The absorbent paper becomes coated with excess ink and solvent. This process is repeated 3 or 4 times until the press is clean (SAIC, 1994).

Number of Use Sites

Most printshops in the United States are small operations. The following was the size distribution in 1992 (Lewis, 1992):

Printing industry, 4/92		
No. of employees	No. of sites	Category
1-4	32152	Small plants
5-9	17365	
10-19	9988	59,505
20-49	6456	Large plants
50-99	2615	
100+	2153	11224

If the PMN-containing ink is known to be used only for high-volume users such as newspapers assume a maximum of 11,224 sites with 25 exposed workers each. For all other cases, assume a maximum of 59,505 sites with 5-6 exposed workers each. News and non-news printers each consume about 50% of the total annual ink production, or 138 x 10^6 kg.yr^{-1}. Thus, the number of sites should be:

$$NS = 11224 \times \frac{(PV \times 100)}{(PPI)(138 \times 10^6)}$$

for news ink. or

$$NS = 59505 \times \frac{(PV \times 100)}{(PPI)(138 \times 10^6)}$$

for other inks. News inks can be distinguished by their low resin content (<15%); this makes the ink cheaper and easier to remove from the paper at the recycling plant, but causes it to rub off on reader's fingers.

Worker Exposure

A. Inhalation

A great deal of information is available on worker inhalation exposure in printshops. Unfortunately, almost all of this exposure can be traced to the high short-term doses resulting from the use of solvents in press cleaning (Hansen, 1988). Inhalation exposures from the ink itself arise from volatilization of the solvent portion of the ink as it dries. If the PMN is volatile, it can be assumed that all of the PMN contained in the ink volatilizes at the printing facility. Using this evaporation rate, the airborne concentration of solvent can be estimated using the standard CEB mass balance approach:

$$C_v = \frac{(1.7 \times 10^5)\, TG}{MQk}$$

where

G	=	Volatilization rate of PMN, $g.sec^{-1}$
T	=	Air temperature (298 K)
M	=	Molecular weight of solvent
Q	=	Ventilation rate (typically 3,500 $ft^3.min^{-1}$)
k	=	Mixing factor (typically 0.5)

In addition to the solvent exposure, there is a potential for exposure to ink mist from high-speed web-fed presses. NIOSH measured ink mist concentrations at a newspaper plant in San Franscisco (NIOSH, 1983), and found a median value concentration of 0.45 $mg.m^{-3}$ (48 samples, range 0.12-3.29 $mg.m^{-3}$). Gikis (1983) found a range of 0.3-6.2 $mg.m^{-3}$. Some inks contain carbon black. There is an OSHA PEL of 3.5 $mg.m^{-3}$ for this material.

B. Dermal

Use standard CEB assumptions. Assume incidental contact, since printers do not immerse their hands in ink but tend to get it on their fingers.

Environmental Releases

A. Air

As noted under Worker Exposures, assume that all of the solvent portion of the ink is lost to the atmosphere as the ink dries. The other components are non-volatile.

B. Water

No water releases are expected from printing facilities.

C. Landfill/incineration

The largest printing presses may have afterburners to reduce solvent emissions to the atmosphere. Some PMN-containing ink will be lost as container residue (1-4%). Most of the ink will be transferred to paper. The paper will eventually be landfilled or repulped. This with result in land disposal of the ink, either as a coating on landfilled paper or in sludge from the paper plant's wastewater treatment unit. However, these releases will not occur directly from the printing facility. There will also be releases of ink from press cleaning. However, the typical ink thickness on a printing plate and the associated blanket cyclinder is only 5 microns (Kirk-Othmer, 1980), so this release is a small fraction of the container residue.

Appendix A: Derivation of a Semi-Empirical Inhalation Model for Ink Manufacture

NIOSH conducted a detailed sampling program at Consolidated Printing Inks in West St Paul, Minnesota, in 1980 and obtained the following results (NIOSH, 1981):

Chemical	Airborne concentration, $mg.m^{-3}$	
	Range	Mean
Ethyl acetate	2.8-183	66
Methyl ethyl ketone	0-131	25
Isopropyl alcohol	11.5-38.4	25
Ethyl alcohol	12.8-266	115
Methyl alcohol	2.3-31.0	17
Methyl isobutyl ketone	0-3.5	2
n-Propyl acetate	0-104	20
Toluene	1.8-37.6	9
Xylene	0-318	46

This data was derived from 109 separate analyses, the results of which are detailed in the NIOSH report. The mole fraction of each chemical in the solvent mixture used at the plant was not specified in the report. However, it can be estimated from the air concentrations if a model for the evaporation process is assumed. Using this procedure, the following average mole fractions were found:

Chemical	Inferred mole fraction in solvent mixture	
	Transfer model	Open surface model
	$C_m \propto MPx_i$	$C_m \propto M^{0.835}(1/29+1/M)^{0.25}Px_i$
Ethyl acetate	0.133	0.145
Propyl acetate	0.053	0.060
Toluene	0.074	0.080
Xylene	0.197	0.208
Ethyl alcohol	0.366	0.343
Methyl ethyl ketone	0.013	0.012
Isopropyl alcohol	0.082	0.082
Methyl isobutyl ketone	0.006	0.007
Methanol	0.076	0.064

where

M = Molecular weight of chemical i
x_i = Mole fraction of i in the solvent mixture
P = Vapor pressure of i

It can be seen that both models lead to similar estimates of the mole fractions. Using these mole fractions, it is then possible to use all 109 data points together to compute a median value of the constant K in the following equations:

$$C_m = KMPx_i$$

$$C_m = KM^{0.835}(1/29+1/M)^{0.25}Px_i$$

The results are:

$$C_m = 0.074MPx_i$$

and

$$C_m = 0.31M^{0.835}(1/29+1/M)^{0.25}Px_i$$

Both of these semi-empirical equations give very similar estimates of airborne concentrations. For a solvent mixture containing 20 mole % xylene, the equation based on the transfer model gives C_m = 71 mg.m^{-3} and the equation based on the open surface model gives C_m = 63 mg.m^{-3}.

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