from: Air Pollutant Emission Factors
April 1970
Contract No. 4-57
22-69-119

4.8 PRINTING INK

Process Description

Ink is a fluid or viscous material of various colors, but most often black, used for writing and printing. Printing inks as supplied to the graphic arts industry are used in much greater volume as compared to writing inks. There are approximately 350 printing-ink manufacturing establishments in the United States today with a production value of over $300 million in 1968.[1]

Printing ink is a mixture of coloring matter, dispersed or dissolved in a vehicle or carrier, which forms a fluid or paste which can then be printed on a substrate and dried. The coloring agents used are most often pigments, toners and dyes, or combinations of these materials. These agents are selected to provide color contrast with the background on which the ink is printed. The vehicle used acts as a carrier for the colorant during the printing operation. In most cases the vehicle serves to bind the colorant to the substrate.[2] Drying oils, petroleum oils, and resins are usually employed as vehicles. However, newer synthetic-resins are becoming increasingly popular because they are quick-drying and have better working properties.[1]

There are four major classes of printing ink. These vary considerably in physical appearance, composition, method of application, and drying mechanism. The four classes are letterpress and lithographic inks, commonly called oil or paste inks; and flexographic and rotogravure inks, which are referred to as solvent inks.

Flexographic and rotogravure inks have many elements in common with the paste inks, but differ in that they are of very low viscosity, and they almost always dry by evaporation of highly volatile solvents.[3]

There are three general processes in the manufacture of printing inks, namely:

1) Cooking the vehicle and adding dyes
2) Grinding of a pigment in a vehicle using a roller mill
3) Replacing water in the wet pigment pulp by an ink vehicle (commonly known as the flushing process).[1]

The ink "varnish" or vehicle consists of resins, drying oils, and/or petroleum oils. This varnish is generally cooked in large kettles at 200-600°F for an average of 8-12 hours in much the same way that regular varnish is made.[7] Most modern kettles are totally enclosed stationary vessels; however, there are still a number of mobile, open kettles being used. Cooking the varnish performs many functions, depending upon the raw materials used and the formulation cycle. These functions include:[4]

1) Polymerization of the oil
2) Depolymerization of the high molecular weight resins at 600 to 650°F
3) Melting and accelerated solution of any solids
4) Esterfication at 450° - 525°F
5) Isomerization
6) Distillation and evaporation

Letterpress, litho, and dry-offset inks are produced in two ways:

1) By mixing preground or flushed pigment concentrates with vehicles, solvents, oils, and compounds.
2) By mixing dry pigments with vehicles and compounds and then grinding them on ink mills.

Some typical ink formulas are given in Table 4.8-1.

Table 4.8-1 Typical Ink Formulas[2]

Letterpress Newsprint Black

10 or 15[a] carbon black
2 or 3 induline toner
85 or 67 mineral oil
3 or 15 mineral oil (low viscosity)

Heat-Set Publication Blue

10 phthalocyanine blue
15 alumina hydrate
65 pentaerythritol resin ester/hydrocarbon solvent
5 polyethylene wax compound
5 aliphatic hydrocarbon solvent (470°F)

Quick-Set Litho Black

16 or 18 carbon black
4 or 6 alkali blue toner
65 or 58 phenolic resin/oil (hydrocarbon solvent, 530°F)
10 or 6 bodied linseed oil
2 or 2 cobalt linoleate
5 or 10 aliphatic hydrocarbon solvent (530°F)

Gloss Letterpress Oleoresinous Red

25 permanent 2B red
5 clay or alumina hydrate
50 phenolic resin/China wood oil
15.5 ester gum/linseed oil
2 cobalt naphthenate
2 lead naphthenate
0.5 eugenol

a) Numbers refer to proportions by weight in mixture.

Mixing of the pigment and vehicle is done in dough mixers of various sizes, or in large agitated tanks which may hold up to 1000 pounds. Grinding is most often carried out in three-roller or five-roller horizontal or vertical mills. Softer, more fluid inks can be ground in colloid mills, sand mills, or ball mills. Dispersion of the pigment in the roller mills is accomplished by shearing forces generated by the differential speed of the rollers as well as by the closeness of roller setting.

Flexographic and rotogravure printing processes require the use of volatile solvents such as low boiling point alcohols, esters, aliphatic and aromatic hydrocarbons, ketones, and water.

Factors Affecting Emission

The quantity, composition, and rate of emissions depend upon the ingredients in the cook, the cooking temperature and time, the method of introducing additives, the degree of stirring, and the extent of air or inert gas blowing.[4]

Particulate emissions resulting from the addition of pigments to the vehicle are affected by the type of pigment and its particle size. Carbon black handling generally causes the biggest particulate problem, and efforts are always made to control this emission with fabric filters.

Emissions

Varnish or vehicle preparation by heating is by far the largest source of ink manufacturing emissions. Cooling the varnish components--resins, drying oils, petroleum oils, and solvents--produces odorous emissions which are very objectionable. At about 350°F the products begin to decompose, resulting in the emission of decomposition products from the cooking vessel. Emissions continue throughout the cooking process with the maximum rate of emissions occurring just after the maximum temperature has been reached.[4]

Compounds emitted from cooking of oleoresinous (resin plus varnish) varnish include water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, terpenes, and carbon dioxide.[4] Some highly offensive sulfur compounds such as hydrogen sulfide, allyl sulfide, butyl mercaptan, and thiphene are formed when tall oil is used in the ink vehicle.

Emissions of thinning solvents used in flexographic and rotogravure inks may also occur. In most of the newer installations, the cooked varnish is pumped to a thinning tank that is equipped with integral condensers and emissions are kept to a minimum. In the older open-kettle operations, however, the thinning operation is carried out near the boiling point of the solvent, and emissions of vapor can be considerable.

Quantitative emission data from ink manufacturing were not found. However, based on published emissions from similar processes such as paint and varnish manufacturing, and discussions with a manufacturer,[5] the factors in Table 4.8-2 were derived. This information is based on information in Chapter 4.6, and no appendix is included in this chapter.

Table 4.8-2. Emissions From Printing Ink Manufacturing

Process	Gaseous Organics[a] lbs/ton	Particulate[b] lbs/ton
Vehicle Cooking		
General	120	
Oils	40 (20-60)	
Oleoresinous	150 (60-240)	
Alkyds	160 (80-240)	
Pigment Mixing		2 (1-4)

a) Emitted as a gas, but rapidly condense as the effluent is cooled, see Reference 6 and 7.

b) Based on Reference 7.

Emissions from the cooking phase can be reduced by more than 90% with the use of scrubbers or condensers, followed by afterburners.[4,5]

Reliability of Emission Factors

Due to a lack of measured emission data, these factors for ink manufacture must be considered questionable. Table 4.8-3 presents the factor ranking.

Table 4.8-3. Emission Factor Ranking for Printing Ink Manufacture

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
0	5	3	8

The current National Air Pollution Control Administration study on printing processes will cover the manufacture of ink, and should provide more quantitative data when it is completed in 1970.[8]

REFERENCES 4.8

1. Larsen, L.M. Industrial Printing Inks. New York, Reinhold Pub. Co., 1962.
2. Inks, Kirk - Othmer Encyclopedia of Chemical Technology. (2nd Edition). 1966, p. 611.
3. Shreve, R.N. Chemical Process Industries (2nd Edition). New York, McGraw-Hill Book Company, 1967. p. 454-455.
4. Chatfield, H.E. In: Air Pollution Engineering Manual, Danielson, J.A. (ed). National Air Pollution Control Administration, Raleigh, N.C. Public Health Service Publication 999-A-P-40-1967. p. 688-695.
5. Private Communication with Interchemical Corp., Ink Division, Cincinnati, Ohio. November 10, 1969.
6. Stenburg, R.L. Atmospheric Emissions from Paint and Varnish Operations. Paint and Varnish Production. p. 61-65 and 111-114. September 1959.
7. Supra, 4.6.
8. Private Communication with L. Lasker. Process Control Engineers Div., National Air Pollution Control Administration, Cincinnati, Ohio. October 1969.