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OVERVIEW OF PRINTING PROCESSES AND CHEMICALS USED

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Abstract

This overview of the use of chemicals in the printing industry identifies potentially detrimental effects on the environment or upon health that merit further investigation. The size and diversity of the industry presents a major problem in the study of the environmental aspects of chemical usage therein. As a prerequisite, therefore, the industry is categorized, in logical fashion, into major printing processes, subprocesses, and supporting processes. For these categories, the current status of utilization by the industry as well as the projected status is estimated. Within these categories, different types of printing operations are discussed, along with their products, in terms of the chemical usage and the possibility of air pollution, water contamination, solid waste, and odor generation. The aim is to indicate the scope of potential problems and their relative magnitude within the industry. New inks and processes are reviewed to show their potential roles and impacts on the environment.

INTRODUCTION

The printing industry applies inks, coatings and varnishes, and solvents to papers, textiles, metals, wood, and plastic materials. Press operations themselves involve emissions to the air. Water use is minimal unless water-base inks are used. Supporting processes (composition, photography, and platemaking), however, involve water contamination, including contamination with metallic salts. The amount of solid waste from printing operations varies widely, and depends upon the size of the plant. Both printing operations and supporting processes involve odors to some extent.

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Odors arise where chemical solvents are evaporated and where chemically reactive inks are exposed to heat.

Five printing processes have been assessed in a recent survey as sources of organic chemical emissions: lithography, letterpress, gravure, flexography, and screen printing (ref. 1). Heat set inks used in lithography and letterpress generally contain 30 to 40 percent solvents. At least half of this solvent is removed in dryers. Gravure and flexographic inks contain up to 80 percent low-boiling solvent, most of which is removed in drying. The major source of emissions in metal decorating (by lithography and screen printing) is the protective coatings put under and over the ink, rather than the ink itself. Many types of inks and paints are used in screen process printing. This process has the smallest total production of paper substrates, but is applied extensively in textile printing. It is definitely a process to study in terms of pollution and health hazards.

The industry prepares image transfer materials, using photographic typesetting and other processes, from which organic compounds, metallic residues, and scrap can be wasted to the air or to water, or to solids disposition.

PRINTING PROCESSES AND AIR POLLUTION

The status, the products, and the chemical usages of the major printing processes are given in appendix A, which also includes these characteristics of the supporting processes. The pollution potential of each of these operations depends upon the nature of the process employed. Printing operations themselves tend to result in emissions of ink solvents and chemicals, some odor generation, and some solid wastes.

Offset lithography transfers ink from an image area, which is essentially at the same level as the nonimage area. The nonimage area is wet by water and the image area is wet by ink only. Water is transferred to the plate first, followed by the ink.

This process customarily employs curved metal plates mounted on a cylinder press. Water used to dampen the plates may contain 15 to 30 percent isopropanol. (If the Dalgren dampening system is used, isopropanol is

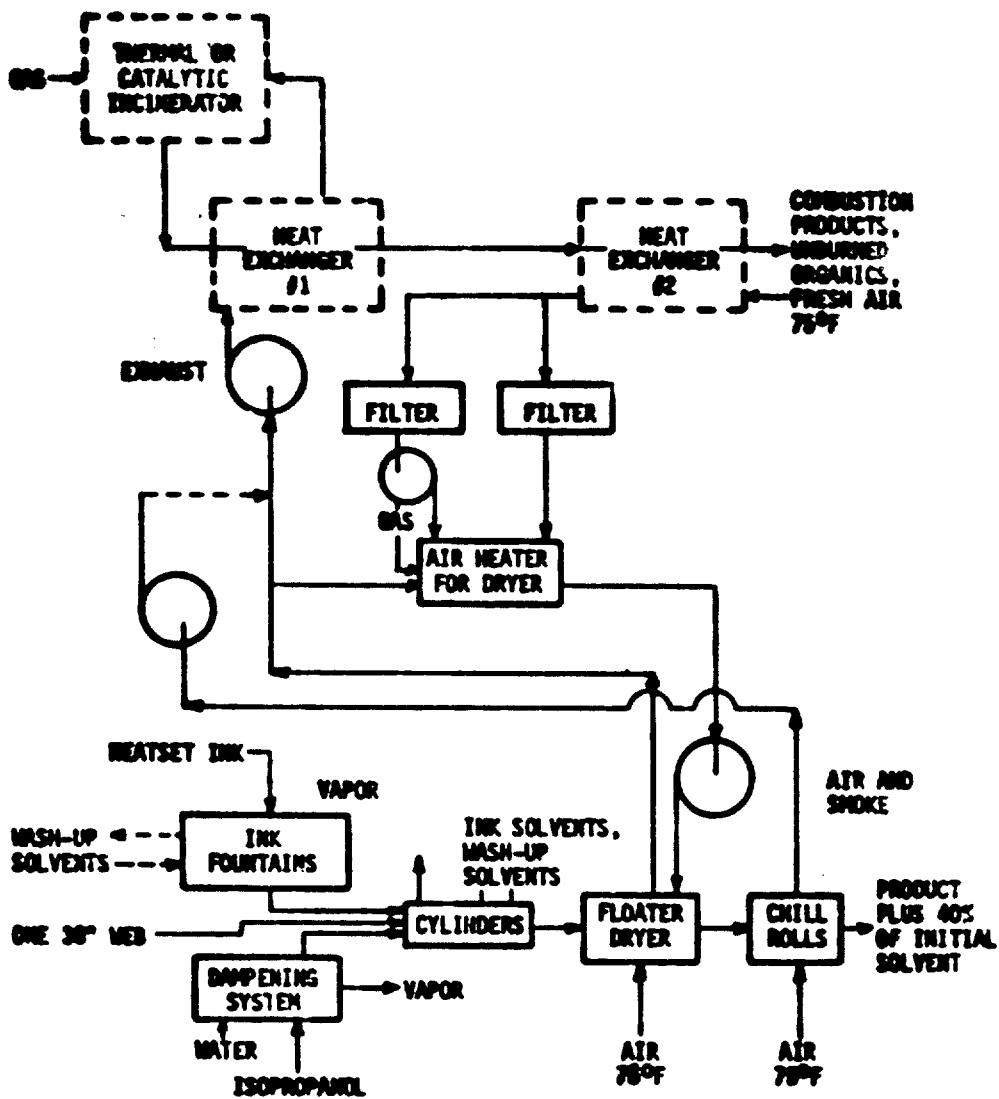
required.) Ink is transferred to the plate, then from the image to a rubber surface on the blanket cylinder, which transfers the ink to the paper. When a web or continuous roll of paper is used, this process is commonly called "web offset."

Figure 1 shows a web offset publication process flow chart in which a 38-inch wide web enters the press at 1,000 feet per minute. With blanket-to-blanket press configuration, the paper is fed between two blankets and two different images are printed simultaneously on the two sides of the sheet. The web passes through several printing units to complete the printing of complete images on both sides, and then it enters the dryer. Leaving the dryer, the paper passes over chill rolls and is then ready for cutting, folding, and finishing. The system exhausts 1,500 to 3,500 standard cubic feet per minute (scfm) of air; it circulates 6,000 to 10,000 scfm through the dryer.

Other configurations are possible. When the paper is printed on only one side, the dryer exhaust rate may be up to 30 percent less than when both sides are printed. A tunnel (floater) dryer is the only type for use when both sides of the web are printed simultaneously. A steam drum dryer is not applicable because of the problem of wet ink contact with the steam drum surface.

Optional additions to the drying process, for emissions control, are shown with dotted lines. While exhaust from the chill rolls is shown entering the dryer exhaust, it could probably be added to the dryer recycle as part of the makeup air, or simply be exhausted without any correction. More information and data are needed to determine whether chill-roll ventilation air needs treatment to eliminate emissions.

The web offset process, when used to print newspapers and business forms, does not usually employ dryers and air pollution control equipment. Emissions are thought to be low because the inks contain very little solvent, porous paper is generally used, and the coverage is much less with text than with pictorial process color work. The total consumption of ink and its associated solvents in newspaper printing has not been separately tabulated. (Census figures exclude a substantial quantity of captive ink made by large printers for their own use.) Nor is there much data on actual emissions.



(Optional equipment shown dotted; letterpress and offset incineration systems are interchangeable.)

Figure 1. Web offset publication.

Sheetfed lithography uses either coated or uncoated paper, and applies low solvent, oxidative-drying inks. Isopropanol is commonly used in fountain solutions. Ink usage is much less than in web offset publication because of the lower feed rate and also because usually only one side is printed.

Letterpress printing transfers ink directly to the paper from the image surface, which is raised slightly above the rest of the plate.

In letterpress newspaper printing, the image is transferred to a mat which can be curved to make a cylinder plate. No dampening solution is used in this process. Washup solvents are, however, used on the press. All other air and organic emissions are from the dryer unless an incinerator is used, in which case the only exhaust is from the incinerator. In a few cases, a catalytic incinerator has been installed in a recycle line for the dryer. This has not necessarily eliminated the need for another incinerator for the exhaust gases.

Letterpress newspaper printing tends to emit relatively inert ink mist and paper dust. The amounts are claimed to be noticeable only in very large installations and can presumably be controlled by an air conditioning system; that is, by moderate filtration of the air. Filters are sometimes placed in ducts located over the presses to remove some of the ink mist and paper dust.

Letterpress publication printing uses different inks for color reproduction, etc. Also, different papers are used, and the inks are not dried by absorption alone. These differences lead to different problems in emission control.

Sheetfed letterpresses tend to use more ink than sheetfed offset presses, because the letterpress ink film is two to three times as thick as the lithographic ink film.

Metal decorating processes transfer the image by lithography or screen to a dried (usually vinyl) lacquer undercoat applied to the metal sheets. Several colors may be applied. After printing, a trailer roller coater puts a varnish coating over the wet ink, and the sheet is dried again. For bottle caps, a thick coating of varnish is put on the outer side and dried. Sheets leaving the 300° F drying ovens may still have 7 to 10 percent

solvents (ref. 2). Coating thickness and solvent content influence the percent solvent in the oven exhaust. Exhaust rates are usually set to limit solvents from 10 to 25 percent of the lower explosive limit. Since the inks themselves contain little solvent, the emissions from lithographic metal decorating are small compared to those from coating application and drying. Solvent is not always exhausted from the roller coating area.

Flexography, like letterpress, transfers ink directly from the plate to the paper or substrate. The plate image area is raised above the rest of the surface. It is made of rubber, however, and alcohol-base inks are used; these characterize the process as flexography. Most flexographic inks contain about 85 percent organic solvent. There are, however, three types of inks: solvent inks, steam set inks, and water-base inks. When solvent inks are used, the product may be steam drum dried or air dried at 140° F, and then passed over chill rolls. It is assumed that more solvent is driven out in the dryer than at the inking area, but the ratio is not known. About 90 percent of the applied solvent is believed to be driven out during and after printing. The remaining 10 percent of the original solvent would evaporate slowly from the solidified vehicle resins on the cool web.

Steam set inks, employed in the "water flexo" or "steam set flexo" process, are low-volatility inks of a paste consistency, which are gelled by water or steam. The vehicles generally consist of a glycol type solvent almost saturated with a resin. The addition of water lessens the solvent power of the glycol, causing the resin to precipitate and gel the vehicle. Further gelling occurs as the solvent penetrates the substrate. This process is used for paper bag printing. No significant emissions have been observed from this process.

Water-base inks are based on aniline dyes, but are now usually pigmented suspensions in water. A dryer is often employed, but since the solvent is water, no emission problems arise.

Brayve processes employ an image recessed relative to the surface of the image carrier. Ink is transferred directly from the image carrier to the paper, film, or other substrate. Since the ink is picked up in the image area and the excess scraped off the nonimage area with a doctor blade,

its viscosity is kept low by a relatively large amount of low-boiling solvent. Control of solvent vapors around the ink fountain is necessary to avoid explosions.

Gravure may be sheetfed or roll fed (rotogravure). Rotogravure is used for coated or uncoated paper, film, foil, and combinations thereof. The process employs either steam or hot air drying at 90° to 150° F. Solvent vapor control is used at the press, the dryer, and the chill rolls. Activated carbon can be used to absorb the vapors, since there are no combustion products or solvent breakdown products in the exhaust. The concentration of solvent in the exhaust from the activated carbon beds is not known, and reliable data are not available.

U.S. plants have recently begun to apply heat-transfer printing to textiles, using the gravure process. The desired pattern is applied to dry-transfer paper, and heated to volatilize it onto the fabric. Current production is some 40 million yards of dry-transfer paper (ref. 9).

Screen printing employs a fine screen for the image area, through which ink or paint can be forced. Nonimage areas are produced by coating the screen to mask off the ink. The amount of organics exhausted into the air depends on the type of ink used. When water colors (for posters), or water-base emulsions (fabric printing) are used, there are no significant emissions. This is also the case if oleoresinous poster inks or alkyd enamels are used. Fast-drying lacquer inks cause significant emissions, however. Evaporation takes place in the printer and the dryer. No information about the percent solvent removed in each operation is available. It is predicted that the solvent will continue to evaporate on the drying racks, although the ink may dry enough to overprint. A study on solvent retention in poly (methyl methacrylate) films--not inks--shows 6 percent residual toluene solvent after 6 months air drying (ref. 3).

Flat and rotary screen printing processes are used to print textiles. Resin-bonded pigments are frequently used (ref. 8).

Thermography is an extension of the printing process, in which the image is raised on a printed page to give the effect of engraving. Either resinous powders are deposited on the print or specially formulated inks that swell on heating are used. Only a few manufacturers who specialize in business or social stationery practice this process.

There are five basic steps, if inks and powder are applied separately. The form is printed as usual by letterpress, or lithography, each having its own characteristic losses of solvents to the air. A raising powder is applied to the printed sheets so that it adheres to the wet ink. Excess powder is removed from the remainder of the sheet. The entire sheet is heated so that the powder melts and fuses with the ink. The sheet is cooled, causing the molten powder to harden. The powdered resins are a potential air pollutant, in their recovery and recycle. Where inks contain the powder, premixed, the process requires only two steps, printing and heating. There is less danger of pollution.

SUPPORTING PROCESSES AND WATER POLLUTION

In addition to the printing processes themselves, there are certain associated processes which are a part of the industry: binding, composition, photography, and platemaking. These appear to generate few problems of air pollution, but are sources of water pollution.

Binding involves the application of hot glues to books, magazines, and commercial forms. Unless solvents are used, the emissions are mostly water vapor. Spiral binding involves the attachment of a plastic binder to specially punched text material. Dusts and waste paper are the principal potential pollutants; chemicals are not involved.

Composition is that step in which the "layout" or model of the copy is converted to press-usable form, either by the hot type method or the cold type method (see appendix A). The hot type method does not employ chemicals. It is used mostly for letterpress printing. In linotype and monotype operations, water may be used for noncontact cooling although most of the machines are air-cooled. Average usage would be about 11,000 liters/day per machine, and a large newspaper would require 20 to 25 linotypes (ref. 10).

Cold type composition includes photo composing, where water is used in the developing and fixing of the output from the typesetting machine. Waste characteristics are similar to the photographic processing wastes to be discussed next. Volumes are generally low, about 5,700 liters/day for one machine, which is adequate for all but the largest printing operations.

Peroxides have been proposed for removal of printing inks (ref. 14). The feasibility of feeding waste paper to farm animals as a source of cellulose has been explored. The presence of polychlorinated biphenyls makes the practice questionable (ref. 15).

Photographic developers and wash solutions usually contain odorous volatile solvents. The odor of acetic acid is often present in photography process areas. This acid has been shown to be harmful to workers' eyes, and is usually removed from the work area with exhaust fans. It is doubtful that the resulting concentrations in the ambient air would have a detectable odor.

Some inks produce odors as the result of chemical reaction during the printing or drying operations, and others, by interaction with the substrate. Most of the odors from inks, however, are those of the solvents employed. No crucial odor problems have been identified at this time.

TYPES OF CHEMICALS USED

A complete listing of the chemicals employed in printing processes would be endless, even if it were possible.* Much of the formulations utilized are bought by the printers from manufacturers who sell under trade names and guarantee performance. The compositions of their formulations are not disclosed. This itself is a problem in the search for potential hazards needing controls and standards. The drying operations employed in printing can decompose certain solvents contained in the inks, so that emissions are not the same compounds as those fed to the system. The extent to which such decompositions occur is known to be influenced by the kind and quality of paper, textile, or other substrate employed.

At the present time, the restrictions imposed on hydrocarbon emissions from stationary sources are expected to affect the printing industry extensively because their chemicals yield these types of emissions. Sulfur oxides and carbon monoxide are not problems. Solid particulates do not generally present problems, but plume opacity will be a problem. Nitrogen oxides may present problems where noncatalytic incineration is employed.

*A partial listing is given in appendix C.

The modification of materials has been rapid and extensive in the last several years so that many printers may have choices of inks and other materials which can effectively control, or at least help control, their pollution problems.

INKS

Letterpress inks are viscous pastes. Vehicles used are slow-drying alkyds or vegetable oil (e.g., linseed oil) derivatives. These inks dry by oxidation and polymerization, during which chemical changes occur that can result in odorous products. Oxidation may be promoted by the addition of reactive ingredients, and these may be volatile or may cause odors. Polymerization may be catalyzed by certain metal salts of organic acids. Although these inks do not dry for several hours, they set (with the assistance of spray powders to protect the printed film) sufficiently to allow satisfactory overprinting through successive units, such as in multicolor work. They are not acceptable, however, for high-speed web operations in letterpress and in offset. These require an ink that will dry in a second or less. Heat-set inks were developed to fill this need. They contain varnishes made by solubilizing solid resins in high-boiling hydrocarbon solvents. A typical heat-set ink may contain 35 to 45 percent of petroleum hydrocarbons with a boiling range of 450° to 550° F. The inks are dried by rapidly removing the solvent as the paper web passes through a drier at temperatures as high as 400° to 500° F. Some thermal degradation, principally of ink and paper components, does occur.

Ink manufacturers have sought a more economical means of printing with high-speed processes than putting solvent into an ink before printing and promptly removing it immediately thereafter. New inks that represent technological advancement beyond solvent reformulation include thermally catalyzed single- and two-component (heat-reactive) systems and ultraviolet-sensitive (photoreactive) systems. These have progressed to commercial feasibility in the United States. Thermally-catalyzed inks contain a pre-polymer, a cross-linking resin, and a catalyst. The catalyst activates at 350° F in the drier and converts the liquid into a solid polymeric film via condensation polymerization reactions. Reaction byproducts are principally

C₁ -C₄ alcohols, moisture, and small amounts of formaldehyde; thus, condensate buildup is prevented in the drier. Overall volatile content of such inks is 20 percent or less of that of the conventional heat-set inks. The smoking tendency is practically nil. Stack odor is said to be reduced (refs. 17,18,19).

Because heat is required for drying, these inks cannot be used on sheetfed presses. The inks have objectionable implant odors. They are at this time expensive (35-80 percent more than heat-set). They are reported to permit buildup of static electricity in the folding operation. More information is needed concerning the extent of applicability and acceptance of this product.

Photoreactive ink systems (UV-inks) consist minimally of one or more monomers and a photosensitizer that selectively absorbs energy. No solvents are contained in the mixture. There are no byproducts since the reaction is addition polymerization. The paper is not heated above 50° C, and a minimum of moisture is lost in the process. The inks do not react until exposed to ultraviolet light; they therefore may be allowed to remain in the fountains and on the rollers for long periods of time. These inks offer advantages to sheetfed lithography; eliminate "set-off," the unintentional transfer of ink to adjacent sheets before the ink has dried completely; eliminate use of powders that are applied to protect an ink film that is "set" but not "dry"; and eliminate the storage of printed sheets for ventilation, required in oxidative drying processes. Disadvantages of this system include cost (75-100 percent more expensive than conventional heat-set inks), the use of expensive UV lamp systems, hazards of UV-radiation to operating personnel, and the formation of ozone by the action of ultraviolet light on oxygen. Conventional commercial procedures will not drink papers printed by this process. This process is, however, at present in commercial use, and more information is required concerning progress in its implementation.

Inks used in lithography are similar to those used in letterpress. Flexography, however, uses inks of low viscosity, made of solvent-resin systems colored either with dyes, pigments, or combinations thereof. The film-forming ingredients vary but usually are soluble in alcohol, alcohol-hydrocarbons, or water. These inks are often employed in metal decorating.

METAL

Some of them, when permitted to come in contact with metals, undergo a chemical reaction and yield a marked odor which is offensive in products, but is not a pollution problem.

Rotogravure inks are low-viscosity solutions of resins in suitable solvents. Air drying presents potential pollution problems. Among the conventional solvents used, toluene and xylene have appreciable odor. To some extent the solvents have been replaced with alcohols having a much milder and less objectionable odor.

Screen printing inks contain a variety of solvents, adhesives, water colors, and emulsifiers. Fast-drying lacquer inks are a serious source of pollution. Among new approaches to pollution control is the use of microwave drying, which tends to evaporate polar solvents without degradation. This technique is indicated for use in gravure and flexography and offers a means of using extensively water-base gravure on plastic substrates. Metal substrates present a problem because they reflect microwaves back to the applicator and damage it. Microwaves are a potential health hazard should leakage occur. Commercial trials in Europe with microwave units for drying inks on cartons have been sufficiently successful that several large European companies reportedly have installed such dryers (ref. 20). The general acceptance of this system is a long time away.

Radio frequency drying is under experimental development. Electron beam drying offers the potential for elimination of solvents and catalytic agents in the inks, but has the disadvantages of degrading the paper under the heavy dosage required, and of generating X-rays, thus necessitating elaborate and expensive operator protection.

The following companies have introduced heat-reactive and/or photo-reactive inks: Bowers Printing Ink Company; Kohl and Madden Printing Ink Corporation; Richardson Ink Company; Roberts and Porter, Inc.; Sinclair and Ballentine; and General Printing Ink Division of Sun Chemical Corporation. Three companies have advanced to the stage of press trials with ultraviolet ink: Sinclair and Ballentine, Jansen Printing (a subsidiary of Holden Industries, Minneapolis), and I. S. Berlin in Chicago.

Further information needs to be brought forth at this time concerning solventless inks. The Lithium Corporation of America introduced in 1971 a

new liquid, polybutadiene-alpha-methylstyrene copolymer resin for solvent-free manufacture of printing inks. Trademarked Lithene-V, the resin series, which was to be available in high and low molecular weights, eliminates the need for solvents because of the low viscosity of the 100-percent reactive materials. The Richardson Ink Company recently introduced its "Duralum Mark V Ink," which should eliminate the need for overprint lacquer when printing aluminum beverage cans. Further information concerning this product would be desirable.

In recent years, there has been a tendency towards increased use of pigments in textile printing. Pigments are molecular aggregates, insoluble in the media to which they are subjected during application and use. They may belong to any chemical class of colors, but they do not contain groups capable of interaction with fibers. Their fixation is achieved, therefore, with the use of a binder which encloses them and provides a bond between them and the fiber. The binders are high-molecular-weight, film-forming materials produced by polymerization of simple intermediates that are initially present in the printing paste. After evaporation of solvent, a thin coherent coating is produced by heating. This film encloses the pigment particles and adheres to the fiber. The rubbing, washing, and drycleaning fastness properties of a pigment print are, therefore, those of the binder film. The most important monomers in modern binders are derivatives of acrylic acid, butadiene, and vinyl acetate. To some extent, urea, melamine, and related products are significant as raw materials for the manufacture of formaldehyde condensates suitable as binders. In pigment printing, white spirit emulsions employed for thickening cause several problems: flammability, odor, and air and water pollution. There is a need for reports of development work underway to reduce or eliminate these problems. The recent development of fully synthetic water-soluble thickeners has enabled the first step to be taken toward avoidance of white spirit. These thickeners are polyacids of very high molecular weight attained by special processes and supplied in various formulations. Their common feature is their unusually high specific thickening action after neutralization.

FABRIC

Wastewaters from printing operations have been shown to contain varying if not high amounts of metals, total suspended solids, and materials

contributing to chemical oxygen demand. Because of this, the extent of effluent reduction attainable through application of the best available technology has been estimated (ref. 10). For example, rotogravure monthly average limitations for effluents have been projected as follows: aluminum, 0.5; COD 5, 30; chromium, 0.5; hexavalent chromium, 0.05; copper, 0.5; pH, 6-9; silver, 0.05; total iron, 1; total suspended solids, 30. All units are grams per cylinder except for pH, which is in conventional units for this determination. More information is needed concerning the application of treatment technology and the extent to which these recommended standards can be met. Costs of complying with these standards also needs to be projected at this time.

SUMMARY AND RECOMMENDATIONS

This review of chemical usage in the printing industry shows the industry to be a dynamic and varied enterprise now going through an era of substantial change, part of which has been motivated by the needs for pollution control and for protection of worker health. The letterpress process now has approximately 35 percent of the market which it supplies and is growing at a rate of about 2-1/2 percent per year. Lithographic processes, however, are enjoying a 12 percent per year annual growth. Flexography is predicted to grow in newspaper and publishing areas. It will be adapted to letterpress and offset processes in the near future. Gravure has about 8 percent of the printing market and it is predicted to capture up to 11 percent in the 1980's. Its growth is about 10 to 12 percent a year. It is concentrated in a few highly specialized plants. The screen process now has 2 percent of the total printing market; it is not expected to grow substantially except in the printing of fabrics, textiles, and carpets. It is definitely, however, a process to study in terms of pollution and health hazards. Composition, photography, and platemaking aspects of the industry are undergoing rapid changes, some of which direct toward more air pollution and less water pollution.

Many of the solvents utilized in this industry are hydrocarbon in nature, and amenable to control by incineration, absorption, and other conventional processes. Industry is, however, beginning to be in the position of

having a choice between the old solvent-based inks and materials and the new non-solvent-based inks employing different processes. Some of the new processes available for use with solventless inks involve new hazards which require some study and evaluation. In this connection, flexible printing, with its vast variety of pigments, dyes, colors, and inks, and its extensive list of proprietary formulations, is almost a special category itself. FABZIC

In view of the extensive innovations carried on in recent years, it is recommended that a conference at this time concentrate on the clarification of the findings of these innovations, on the extent of commercialization of any processes or procedures that tend to alleviate pollution problems, and on thoroughly delimiting through discussion involving experts the advantages and disadvantages of the approaches. The industry should be re-evaluated at this time in terms of its future and current trends. The program participants must, if this recommendation is adopted, include personnel of companies supplying materials--inks, papers, other substrates--and equipment peculiar to the industry. Less factual information is available concerning air pollution than concerning water pollution, primarily because more extensive sampling and testing has been performed on wastewater samples. It is recommended that part of the sessions of the conference focus upon new measurements of the effluents and emissions from printing processes.

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**APPENDIX A
PRINTING PROCESSES, PRODUCTS, AND CHEMICAL USAGE**

Process	Stats	Products	Chemicals
1. Lithography (metal printing) A. Sheet-Fed Press Types Platen Cylinder Composition Handset Machine Linotype Letter Linocut Linocut Linocut	50% of market; Avg. annual growth 1955-72: 2.5% (6)	Gold stamping Die cutting Forms Stationery Pamphlets, brochures Books Magazines Newspapers Taps Labels 4-color process HCR forms*	Ink - Dry by absorption, chemical oxidation, and evaporation. Solvent Gelatin Varnishes Resins Retarders (optional) Type wash* Press and roller wash* Spray powder Flame dryers Steam ink Dry by absorption Process ink Dryers Varnishes Resins Retarders Type wash Press and roller wash Spray powder (to prevent offset) Flame dryers
B. Web-Fed Print from: Densitograph Microtyping Photographic plates		Newspapers Books Magazines Continuous forms Snap-report forms	Steam ink Dry by absorption Process ink Dryers Varnishes Resins Retarders Type wash Press and roller wash Spray powder (to prevent offset) Flame dryers
2. Planography (metal printing) Print from rubber or photopolymer plates. Galleys plates	Predicted to grow in newspaper and publishing industry. (1) Will be adapted to laserpress and offset processes in future.	Plastic film Fold bags Milk cartons Cardboard cartons Gummed tape Bread and candy wrappers Newspapers and magazines on increase	Water-based emulsified ink Ultraviolet ink
3. Lithography (Planography) A. Sheet-Fed	50% of market Avg. annual growth 1955-72 - 10.2% (5) 50% of total commercial printing in the next 5 years. (8) Rapidly growing at rate of 8-9% per year. (7)	Small newspapers Greeting cards Slips Forms Labels, tags HCR papers Forms Stationery Brochures, booklets Magazines Books	Photocopying Developer coatings Sensitizers Developers (aqueous) Gum arabic (preservative) Image removers Subtractive developers for subtractive plates Plate cleaner (to remove toner)* Carbon ore (see annual census lists established by GMA) Slurry lamps

Newspaper industry - largest single industry in terms of \$ - produced \$14.8 billion in 1976.

* Identifies possible toxic materials.

APPENDIX A (con.)

Process	Status	Products	Chemicals
2. <u>Lithography</u> (Planography)			
A. <u>Sheet-Fed</u> (con.)			<p><u>Plate materials</u> Aluminum - 95% of all;* Zinc; Brass; Copper; Chrome plate; Steel</p> <p><u>Pressroom</u> Gum arabic Fountain solutions to maintain pH 1) glycerine and 2) alcohol Powder spray dryers to prevent offset Flame dryers to set ink Roller and blanket wash Rubber rejuvenator</p> <p><u>Inks</u> Reducers*, varnishes*, driers* Retarders (to prevent "skin")* Fluorescent inks* Metallic inks Regular inks* Plastic ink Foil ink</p>
B. <u>Web-Fed</u>	Presently growing at 10-12% per year. (7) Will amount to 8% of total litho commercial printing in next 5 years. (8) Faster growth rate, but is starting from a smaller base.	Newspapers Magazines Books Felts Plastics Metal decorating Continuous forms Snap-apart forms	<p><u>Pressroom</u> Same as sheet-fed</p> <p><u>Inks</u> Process inks Ultraviolet (UV) inks Heat-reactive inks</p>
4. <u>Gravure</u> (Intaglio)	8% of printing market. Predicted to capture 11% in 1990's. Fastest growth rate of 10-12% per year. (8)		<p><u>Platemaking</u> Etches (25% nitric acid) Fixers Developers</p>
A. <u>Decorative and specialty</u>	Highly concentrated in few highly specialized plants.	Announcements Invitations Social stationery Business stationery Government currency Government bonds Postage stamps	
B. <u>Photogravure</u>	Slow and expensive, limited use. Mostly done by hand.	Fine paintings Photographs	<p><u>Plates</u> Prepared photographically and etched chemically.</p>
C. <u>Rotogravure</u> Printing done by rotary presses. Paper fed from rolls (web) ink in liquid form.	Most predominant of gravure processes. Fastest growth rate of all printing processes of 12-16% per year. (7)	Catalogs Magazines Wallpaper Fabrics 17% specialty printing(4) 27% packaging 80% publications	<p><u>Cylindermaking</u> Semiauto gravure cylinder etching machines</p> <p>Electronic color spacers</p>

*Identifies possible toxic materials.

APPENDIX A (con.)

Process	Status	Products	Chemicals
<p>4. <u>Gravure</u> (Intaglio)</p> <p>C. <u>Rotogravure</u> (con.)</p>		<p>Wood grain coverings Vinyl sheeting Decorative high-pressure laminates Foil</p>	<p>Electronic gravure cylinder engraving</p> <p><u>Pressroom</u> Electronic ink transfer process</p> <p><u>Inks</u></p>
<p>For more information</p> <p>Gravure Research Institute Gravure Technical Association</p>			
<p>5. <u>Screen-Process</u></p>	<p>2% of total printing market (B)</p> <p>Not expected to grow substantially.</p> <p>Definitely a process to study in terms of pollution and health hazards</p>	<p>Posters Billboards Glass bottles and jars Book covers and ribs Toys Furniture Fabrics Oilcloths Glass plate Felt banners Printing circuits Dials Metal Clay</p>	<p><u>Screenmaking</u></p> <p><u>Pressroom</u> (solvents, sprays, etc.) Lacquer thinners Mineral spirits Reducers</p> <p><u>Inks</u> Oil paints, enamels, poster paints, lacquers, varnishes, vinyl (fusion), metallic, plastic inks, adhesives</p> <p><u>Washup and cleaning</u></p> <p><u>Inks</u> Resinous powders, e.g., embossograph Hi Flo neutral powder</p> <p>Formulated inks</p> <p>Flourescent powders</p>
<p>6. <u>Thermography</u> A process used to raise the image on a printed page after being printed by letterpress or litho process. Gives the effect of engraving</p> <p>Process uses either a resinous powder which is deposited on ink after printing or specially formulated inks that react to heat causing ink to expand or "swell" thus raising the image from the paper.</p>	<p>Process performed by relatively few manu- facturers who special- ize in social and busi- ness stationery</p>	<p>Announcements Invitations Social and business stationery</p>	<p><u>Inks</u> Resinous powders, e.g., embossograph Hi Flo neutral powder</p> <p>Formulated inks</p> <p>Flourescent powders</p>
<p>7. <u>Binding</u></p> <p>A Bookbinding</p> <p>B Magazine binding</p>			<p>Hot glues</p> <p>Hot glues</p>

* Identifies possible toxic materials.

APPENDIX C
TYPES OF CHEMICALS USED IN THE PRINTING INDUSTRY

INKS

SOLVENTS

Aromatic Compounds

Benzene
Toluene
Nylene
Ethylbenzene
Turpentine
Stoddard solvent
Versol
Biphenyl
Orthophenylphenol
Bis-zoric acid
Phenol

Aliphatics

Pentane
Isooctane
Naphthenes
Mineral spirits
Naphthalene
Heavy naphthalene

Oxygen Containing Compounds

Methanol
Ethanol
Propanol
Isopropanol
Butanol
Isobutanol
Ethyleneglycol
Ethyleneglycol acetates
Ethyleneglycol butyrates
Acetone
Methyl Ethyl Ketone
Methyl phenyl carbino
Acetophenone
Acetic Acid
Diethylene glycol
Urea
Glycerol

Chlorinated Compounds

Trichloroethylene
Trichlorooctane
Methylene chloride
Chlorinated paraffins
Chloroenzines

Pigment Bending Agents

Melamine-formaldehyde
Polyacrylic acetate

Viscosity Stabilizers

Sodium hexametaphosphate
Tetra-sodium pyrophosphate

Antifrosting Agents

Diethanolamide

Acid-Producing Agents

Acetic acid
Citric acid
Formic acid
Tartaric acid

Thickening Agents

Alginates
Cellulose ethers
Acrylamide - N-t-butylacrylamide copolymer
Dextrin
Phosphoric acid esters of onyethylated wan-alcohols
Fatty acid esters of ethylene glycol
Ethylene oxide polymers with starch
Guar germs
Gum arabic
Gum tragacanth
Polyacrylamide
Polyacrylic acids
Starches
Biosynthetic natural gums

Pigments*

*A comprehensive list of pigments is given in *Textile Chemist and Colorist, Products 74*, Vol. 5, No. 10A (October 1973), pp. 29-96.