TOXICS USE REDUCTION INSTITUTE

THE MASSACHUSETTS TOXICS USE REDUCTION INSTITUTE

SUBSTITUTION CASE STUDY:

ALTERNATIVES TO SOLVENT AND PETROLEUM-BASED INKS

Technical Report No. 5 1993

University of Massachusetts Lowell

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University of Massachusetts Lowell

May 1993

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INSTITUTE

The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to governments to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

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PREFACE

As more companies search for and develop environmentally safer production processes the need for information on cleaner production processes is on the rise. To promote knowledge of the availability of technically and economically feasible alternatives to toxic chemicals and products in the workplace, the Toxics Use Reduction Institute sponsors "substitution" studies. A substitution study focuses on input substitutes or process changes that eliminate or reduce the use of a toxic chemical or product and replace it with safer alternatives. The need for substitution studies arise because input substitution in manufacturing is a complex process. Factors that make input substitution a complex process include changes to product quality, product profitability, environmental and human health, and roles of employees. All of these factors must be included in a substitution analysis to understand the effects of input substitution. The purpose of the substitution studies is to provide an understanding of safer chemistries, processes, and products that are on the market and the benefits and costs to a manufacturer of switching to one of these alternatives.

The substitution studies prepared for the Toxics Use Reduction Institute are designed to provide information to technical assistance programs, manufacturers, and government toxics use reduction and pollution prevention programs on technically and economically feasible safer alternatives to toxic inputs. This report was prepared by the Tellus Institute for the Toxics Use Reduction Institute. The opinions expressed in this report are those of the authors and not necessarily those of the Toxics Use Reduction Institute.

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1. Introduction

Printing inks are a diverse group of petroleum and solvent-based materials. Components of ink vary with ink color, the paper or other material (also known as substrate) which is to be printed, the type of printing process used, and other characteristics specific to the desired end product. For example, inks used for printing bumper stickers must resist fading and be weather-proof, inks used for consumer packaging must be bright, and generally, inks must dry so they are smudge and rub resistant.

Section 2 of this report presents the major commercial printing processes. The characteristics of the inks used for processes which dominate the Massachusetts commercial printing industry and less toxic or non-toxic alternatives to these inks are presented in Sections 3 and 4.

2. Printing Processes

The commercial printing industry may be categorized by the various types of printing processes. The five major processes in order of increasing national and state market share are: screen, letterpress, flexography, gravure, and lithography. Each process uses a different method to transfer the printed image onto the paper or substrate that is to be printed, as well as different equipment and type of inks. Product quality and cost are the major factors determining which process is used for a particular application.

Screen printing, also known as silk screening, is the most versatile printing process as it can print on many substrates including paper, wood, glass, fabric, plastic, and metal. A stencil on the screen protects the areas that are not to be printed so that when ink is applied to the screen, it will only pass through the non-protected areas which comprise the image. As screen printing is considered a more specialized form of printing and is not widely used (it accounts for approximately 7% of all U.S. commercial printing)[1], alternative inks used for this process are not included in this paper.

Letterpress is the oldest printing method. Printing is accomplished by using plates in which the image or printing areas are raised above the non-image areas. When ink is applied to the plate, the ink rollers only touch the raised areas. The inked image is then transferred directly onto the paper. While previously plates were made using cast iron type, today typesetting is done primarily using computers. Since changes to the plate can be easily made, letterpress is used for printing literature that requires constant updating such as price lists, timetables and directories. Letterpress has been used for printing newspapers and magazines although many publications are switching to lithography. Books and advertising brochures can also be printed with letterpress. Since letterpress printing does not have a large market share (approximately 11% in the U.S.)[2], alternative inks used for this process are not included in this paper.

Web presses can be further classified based upon the presence or absence of a dryer. Heatset webs have a drying unit at the end of the web which dries, or sets the ink. Thus, the inks used by these webs are known as heatset-inks. Webs that do not have this drying unit use non-heatset inks that dry by absorption into the paper. This latter type of ink is also used by sheetfed presses.

3. Lithographic Inks

The components of ink include pigments which provide the color and consist of organic or inorganic materials, resin vehicles which act as carriers of the pigment, solvents or other fluids to dissolve the resins and control the body and viscosity of the ink, and other additives that impart other characteristics to the ink depending upon its application. Waxes, lubricants, and driers are some of the additives found in ink.

Vegetable oils were the original vehicles used in lithographic inks. As high-speed presses were introduced, vegetable oil-based inks fell out of favor because the inks required too much time to dry. Quicker drying petroleum oil inks eventually replaced the vegetable inks.

Today, petroleum oils are a component of all lithographic inks, serving as a vehicle for the pigment and providing body and viscosity to the ink. These oils are composed primarily of normal paraffins and naphthenic fractions of a petroleum distillate.[7] The presence of these oils may pose potential environmental and worker health and safety concerns if improperly used or stored. In the workplace, skin exposure to petroleum oil-based ink may cause skin irritation and inhalation may cause dizziness and drowsiness. The Occupational Safety and Health Administration (OSHA) has various housekeeping requirements which are designed to minimize exposure to employees. There are currently no specific OSHA permissible exposure levels (PEL)* for lithographic inks. However, the PELs for oil mists (5 mg/m^3), naphtha solvents (100 ppm), and petroleum distillates (400 ppm), and others have been used for comparative purposes.

Due to the volatility of petroleum oils, volatile organic compounds (VOCs), which are precursors to ground-level ozone formation, may be generated from the use of inks. Ozone causes lung, eye, and other mucous membrane irritation and can cause permanent lung damage. While the VOC content of printing inks is not regulated, emissions of VOCs are regulated by individual states and the U.S. EPA. In Massachusetts, a commercial printer is considered a major source of air emissions if greater than 50 tons/year of VOCs are emitted. The potential to emit is calculated based upon the maximum capacity of the equipment, assuming that the equipment runs 24 hours per day and 365 days per year or as limited by an enforceable operating permit through limitation of operating hours or production unit quotas. The amount of ink oil retained in the printed product and the amount of discarded solvents

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*The PEL is a time-weighted average concentration for an 8-hour workday and 40-hour workweek, to which nearly all workers may be repeatedly exposed without causing an adverse health effect.

18%, but the ink manufacturers could not produce an acceptable ink with this soy content.[10] Thus, although it is the dryer that causes the generation of VOCs, it is also what limits the soy content. Substituting 10% soy oil for petroleum oil can however help reduce VOC emissions - soy heatset inks can provide a 16.6% reduction in VOCs as compared to conventional heatset inks.[11] This reduction however is accompanied by a 5 to 8 percent increase in the cost for ink.[12]

TABLE 1. SOY CONTENT OF PRINTING INKS RECEIVING ASA SOY SEAL

INK TYPE	MINIMUM SOY CONTENT
HEATSET	10%
NON-HEATSET	20%
NEWSPRINT	55%
FORM	40%

3.2 Non-heatset inks

These inks are used both on sheet-fed presses and non-heatset webs. Because these presses do not have dryers, the inks instead dry both by absorption into the paper and by oxidation, absorption of oxygen from the air which causes the ink to harden. The VOCs in the ink oils are not volatilized as much as heatset inks due to the absence of a dryer. Approximately 5% of the VOC content will be released during printing operations; the remainder stays in the ink.[13]

The soy or vegetable content of these inks is dependent upon the type of paper being printed. Uncoated stock can have a higher content of these oils as the paper is more absorbent. The soy content of inks used on coated stock is limited because coated stock is less absorbent; instead, oxidation of the ink plays a more important role in drying. Color is another important factor dictating soy content. Black inks, which are slower drying, can only contain approximately 20% soy oil while some of the other colors can contain 25% soy. To display the Soy Seal, non-heatset inks must contain a minimum of 20% soy oil by volume.

Substituting the petroleum oil in non-heatset inks with either soy or other vegetable oil-based inks involve trade-offs. The positive attributes of soy and other vegetable inks include reduction of VOC emissions associated with printing operations. Because soy oil is clearer than petroleum or linseed oils, in some applications soy oils can actually provide a better print quality and brighter appearing colors.[14] Some users of soy ink report better ink pickup and transfer, resulting in shorter production start-up time and less waste. The

3.4 Form inks

Business forms are printed on non-heatset web presses. As with newsprint inks, form inks can contain a higher percentage of soy or vegetable oil since the paper used for printing business forms is absorbent. Inks using the Soy Seal must contain a minimum of 40% soy oil.

3.5 Radiation curing inks

Radiation curing inks are another alternative to oil-based lithographic inks. There are two types of radiation curing inks that contain no solvents: ultraviolet (UV) and electron beam (EB) inks. UV inks consist of one or more monomers and an initiator which, on exposure to UV radiation, release free radicals that polymerize or "cure." These inks can be used both on sheetfed and web presses. Because the ingredients in UV inks are expensive, they are approximately twice the cost of conventional solvent-based inks. Therefore, their use has mostly been limited to luxury packaging such as liquor and cosmetic boxes, metal decorating, and screen printing.[22] The main advantage to using UV inks is that they contain no solvents and therefore decrease worker exposure to solvents in the printing industry. Because these inks do not set until exposed to UV light, the ink does not dry up on the press, reducing press cleaning time. However, the reaction of UV light with oxygen forms ozone and the UV lamp must be properly shielded to prevent employee exposures. The UV unit also poses an additional capital expenditure.

EB inks are similar to UV inks, but are not as expensive. As with UV inks, their use decreases worker exposure to solvents since these inks are formulated without solvents. However, x-rays are created by the use of EB inks so proper operation protection is needed. The major disadvantage to EB inks is the high capital cost of equipment.[23]

4. Flexographic and Gravure Inks

These two inks are discussed together as their chemical and operational properties are similar. Gravure inks are rapid drying inks which must have the proper viscosity in order to be pulled down from the sunken area of the plate containing the ink. Flexographic inks are also quick drying and have a viscosity similar to that of the gravure inks.

Conventional flexographic and gravure inks commonly contain alcohols such as ethyl alcohol and isopropyl alcohol. These alcohols are flammable and pose worker health and safety risks including irritation to the eyes and upper respiratory tract, headaches, drowsiness, and dizziness. The OSHA PEL for both alcohols is 1000 parts per million (ppm).[24,25]

Most printers using flexography and gravure have substituted water-based inks for the alcohol-based inks due to concerns with worker health and safety, flammability, and high present an environmental concern as well. Petroleum-based inks are volatile and cause VOC emissions, precursors to the formation of ground level ozone.

To reduce the VOC content of inks, manufacturers have substituted petroleum oil with vegetable oils such as soy, linseed and tung. The characteristics of these substitutes are summarized in Table 2. The degree to which these oils can replace petroleum oils depends upon the type of press used for a specific job, the type of paper being printed, and the color of the ink. Soy and other vegetable inks dry slower than conventional inks, especially if the paper is not very absorbent. Therefore, more absorbent paper, such as newspaper and business forms, can use inks with greater vegetable oil content whereas coated stock, which is not very absorbent, cannot use an ink with a high soy or other vegetable oil content. Heatset inks can tolerate the lowest amount of soy oil as the dryer temperature required to dry such an ink would scorch the paper.

Several positive effects have been attributed to the use of soy oil. Soy oil is lighter in color than petroleum oil; as a result, colors appear brighter. Other advantages include greater stability, less tendency to develop a skin if the ink sits around for awhile, less susceptibility to piling (ink build-up on the printing plate), and better color control.[29]

Another advantage to using soy or other vegetable ink is the resulting reduction in VOC content of the ink. However, the inks that generate the most VOCs upon use, heatset inks, can tolerate the smallest soy or vegetable oil content. The VOCs contained in other offset inks are mostly absorbed into the paper; little is released into the environment.

Several experts in the printing industry also noted that printing inks are not the major source of solvents or VOCs in the industry: fountain solutions contain glycol ethers, solvents are used to clean the presses and blankets, and coatings may be solvent-based. These sources represent far greater uses of solvents and generation of VOC emissions.

In sum, trade-offs exist in using soy or vegetable inks versus conventional petroleum oil-based inks. Soy and other vegetable-based inks provide several beneficial printing properties but dry slower than petroleum-based inks. Certain types of lithographic inks are more expensive if the petroleum oil is substituted with soy oil. However, it appears that these price differences are diminishing.

UV and electron beam inks are another alternative to conventional inks. These inks contain no solvents, thereby eliminating VOC emissions and worker exposure to ink solvents. However, the cost of these inks are higher and capital expenditures for new equipment is required.

Gravure and flexographic inks contain alcohol-based solvents. Due to environmental concerns and insurance costs associated with use of these inks, the solvents have largely been replaced with water. Benefits of this substitution include elimination of hazardous waste disposal associated with inks, reduced insurance costs, and better print quality.

TABLE 2. SUMMARY OF ALTERNATIVES TO PETROLEUM- AND SOLVENT-BASED LITHOGRAPHIC, FLEXOGRAPHIC, AND GRAVURE INKS

Alternative Ink Product	Ink Attributes	Technical Advantages	Technical Disadvantages	Capital Costs	Operating Costs	Product Quality	Environmental and Occupational Health
Lithographic Soy-Based Heat-Set Web Press Inks Inks include 10% soy oil content by volume and 35-40% petroleum oil by weight.	Inks must withstand high drying temperatures (200-300° F), dry quickly, & have the proper viscosity & tackiness.		Slower drying time.	No capital costs.	Soy-based inks are 5-8% more expensive than conventional inks.	Similar quality.	Lower VOC emissions and worker exposure to petroleum oils.
Lithographic Soy-Based Non-Heat Set Inks Inks include 20-25% soy oil content by volume.	Inks must dry by absorption and oxidation, dry quickly, and produce bright clear colors.	In some applications, better print quality, brighter appearing colors, better ink pick-up, and transfer.	Slower drying time.	No capital costs.	Soy-based inks are slightly more expensive than conventional inks.	Similar quality, with brighter colors and improved clarity.	Lower VOC emissions and worker exposure to petroleum oils.
Lithographic Soy-Based Newsprint Inks Inks include 55% soy oil content by volume. Oil-based newsprint inks can be completely replaced by soy or vegetable oils.	Inks must dry solely by absorption.	Produce high quality color printing.	Slower drying times.	No capital costs.	Soy-based color inks are slightly more expensive, but can produce more copies/pound of ink, minimizing cost differential. Soy-based black inks cost 0-30% more than conventional inks.	Higher quality color printing and similar quality black inks.	Lower VOC emissions and worker exposure to petroleum oils.
Lithographic Form Inks Inks include 40% soy oil content by volume.	Form inks are used in non-heatset web presses and must dry solely by absorption.		Slower drying time.	No capital costs.		Similar quality.	Lower VOC emissions and worker exposure to petroleum oils.
Lithographic Ultraviolet Radiation (UV) Curing Inks For use in sheet-fed and web presses.	UV inks consist of one or more monomers and an initiator that are cured by UV light.	Press cleaning time is reduced because no solvents are used.		High capital costs to purchase UV equipment.	UV inks are twice as expensive as conventional inks.	Print quality is not as clear.	VOC emissions and exposure to petroleum oils are eliminated. Workers must be protected from ozone emissions and exposures to the UV lamp. Greater energy use. UV inks make recycling of the paper more difficult.

TABLE 2. SUMMARY OF ALTERNATIVES TO PETROLEUM AND SOLVENT BASED LITHOGRAPHIC, FLEXOGRAPHIC, AND GRAVURE INKS (continued)

Alternative Ink Product	Ink Attributes	Technical Advantages	Technical Disadvantages	Capital Costs	Operating Costs	Product Quality	Environmental and Occupational Health
Lithographic Electron Beam (EB) Radiation Curing Inks For use in sheet-fed and web presses.	EB inks consist of one or more monomers and an initiator that are cured by an electron beam.	Press cleaning time is reduced because no solvents are used.		High capital costs to purchase EB equipment.	EB inks are more expensive than conventional inks.	Print quality is not as clear.	VOC emissions and exposure to petroleum oils are eliminated. Workers must be protected from exposure to x-rays. Greater energy use. EB inks make recycling of the paper more difficult.
Flexographic and Gravure Water-Based Inks	Flexographic and gravure inks must be rapid drying and have the proper viscosity.	Presses can run faster in some cases.	Un-satisfactory images may be produced, requiring new capital equipment.	Low to moderate to purchase printing cylinders and plates.	Lower due to faster press speed, reduced hazardous waste disposal costs, and reduced insurance costs.	Similar product quality with new capital equipment.	Eliminate the use of alcohol- and other solvent-based inks reducing VOC emissions and worker exposures. Greater energy use for drying.

Endnotes

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