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The Development of Substitute Inks and Controls for Reducing Workplace Concentrations of Organic Solvent Vapors in a Vinyl Shower Curtain Printing Plant

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During the summer of 1994, football players at a practice field reported noxious odors in the area. Ohio Environmental Protection Agency (OEPA) investigations of industries surrounding the field included a printing facility producing vinyl shower curtains with screen-printed designs. Though not the source of the odor, they were discharging volatile organic compounds directly to the environs in violation of OEPA regulations. To achieve compliance they installed a catalytic oxidizer for treating discharged air. Due to high equipment costs, the capacity of the installed catalytic oxidizer resulted in a substantial reduction in discharged air flow rates and increased solvent vapor concentrations within the workplace. Vapor levels caused worker discomfort, prompting a request for assistance from the Ohio Bureau of Workers Compensation. The vapor concentrations were found to exceed NIOSH, OSHA, and ACGIH[®] acceptable exposure levels. The workers were then required to wear organic vapor removing respirators full-time while printing as a temporary protective measure. The company requested NIOSH assistance in finding methods to reduce solvent vapor concentrations. NIOSH studies included the identification of the sources and relative magnitude of solvent emissions from the printing process, the design of controls for the emissions, and the development of substitute inks using non-photochemically reactive solvents. The new ink system and controls allowed OEPA removal of the requirement for the treatment of discharged air and substantial increases in dilution ventilation. Increased ventilation would permit reduction in worker exposures to less than 1/3 mixture TLV[®] levels and removal of requirements for respirator usage. This solution was the result of a comprehensive review of all facets of the problem, including OEPA regulations. It also required cooperative work between the

company and federal, state, and local governmental agencies.

Keywords Vinyl Printing Inks, Single-Pass Ventilation, VOC, Organic Solvents

INTRODUCTION

Background

In the summer of 1994, members of a football team complained of noxious odors present at their practice field in an industrial neighborhood of Cincinnati, Ohio. The Ohio Environmental Protection Agency (OEPA) proceeded to determine the source(s) and significance of the odor. In the course of a review of industries surrounding the field, the OEPA inspected a printing company producing screen-printed vinyl shower curtains. Though this company was not the source of the odor in question, its discharge of organic solvent vapors to the environs violated OEPA volatile organic compound (VOC) regulations. To correct that problem, the company installed a catalytic oxidizer to treat air exhausted from the facility. Unfortunately, its use resulted in a reduction in the amount of air discharged by approximately two-thirds, resulting in much higher concentrations of solvent vapors in the workplace atmosphere.

Employees complained of mucus membrane irritation, dizziness, and chest pains. The company requested the assistance of the Ohio Bureau of Workers' Compensation (OBWC) in evaluating those health concerns. Initial measurements showed that solvent vapor inhalation exposures of the printing workers exceeded Occupational Safety and Health Administration (OSHA), American Conference of Governmental Industrial Hygienists (ACGIH[®]), and National Institute for Occupational Safety and Health (NIOSH) acceptable concentration levels. In some cases, the time-weighted average (TWA) mixture threshold

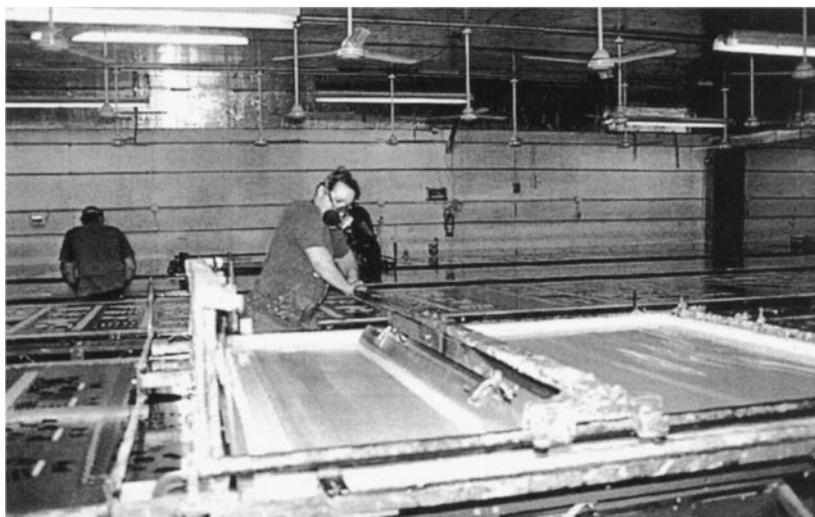


FIGURE 1

Worker squeezes ink/solvent mixture through printing screen, using rubber-edged squeegee blade.

limit value (TLV[®])⁽¹⁾ was exceeded by approximately 300 percent. The company instituted the full time use of organic vapor removing respirators during printing operations. It also requested that NIOSH assist them in finding methods to reduce occupational exposures to the solvent vapors.

Process Description

Printing was carried out on four printing tables 7 ft wide \times 150 ft long, which were located side by side in a room approximately 50 \times 200 \times 12 ft. Prior to printing, sheets of plasticized polyvinyl chloride approximately 6 ft wide \times 0.006 in thick were rolled onto each table. Movable screen-printing units, having approximately 6.3 ft \times 7 ft polyester printing screens, were

used to apply ink onto the vinyl at regular intervals (24 per table) along the length of each table (see Figure 1). Solvents were used to dilute the ink to the desired viscosity for printing and for maintaining that viscosity during printing. Several printer units followed each other in the process with an approximately 40 s time interval, each depositing a different color (up to six colors) in the design. The printing units moved down one table and back on an adjacent table until all vinyl was printed (see Figure 2).

After all colors were printed, the vinyl sheet was rolled up and a new one was rolled onto the table. The printed vinyl was moved to an adjacent room where hooking strips were attached to curtain tops with a radio-frequency heat-sealer and the curtains were cut, folded, and packed. Approximately 1800 six-color shower



FIGURE 2

Printer units on right work along table to far end laying down printed images (visible in foreground), turning around and following printer unit on left.

curtains could be produced in a day. Approximately 10 workers were employed in the printing operation, working throughout an 8 h workday with a 30–40 min lunch break. Payment was associated with production yield, resulting in a fairly intense working pace.

Scope of Study

Our goal was to provide affordable methods for reducing the worker solvent vapor exposures to levels that would not require the use of respirators. The study included:

- identifying the sources and magnitude of solvent vapor emissions
- designing controls for reducing solvent vapor emissions
- considering various methods of removing solvent vapors from workplace atmosphere
- reviewing OEPA regulations controlling discharges of solvent vapors from the facility, seeking more feasible approaches to lowering worker exposures
- developing substitute ink systems that allowed the elimination of the need for removing solvent vapors from air exhausted from the facility
- evaluating the worker exposures after various process changes
- designing a cost-effective, single-pass HVAC system, increasing workplace ventilation

Except where noted, all estimates of costs for materials and equipment are in 1997 U.S. dollars and represent technology available in 1997.

MATERIALS, METHODS, AND RESULTS

Occupational Exposure Measurements

OBWC personnel measured workplace solvent vapor exposures for individual workers engaged in printing under condi-

tions reported by the workers to be typical. Sampling occurred while the worker was working in the printing room and was discontinued when the worker left the area. In some cases individual workers did not spend the complete workday in the printing room. All workers engaged in printing were not always monitored, due to a limitation in the availability of sampling equipment, equipment malfunctions, or a lack of need for sampling all personnel.

Samples were collected on small bed charcoal tubes (SKC, Inc.) with the inlet in the employees' breathing zones (around the head and neck). The samples were analyzed by an American Industrial Hygiene Association (AIHA)-accredited laboratory using the following analytical methods: butyl acetate, NIOSH 1450; acetone, cyclohexanone, methyl isobutyl ketone, methyl propyl ketone (MPK), NIOSH 1300; diacetone alcohol, NIOSH 1402; dipropylene glycol monomethyl ether (DPM) and propylene glycol monomethyl ether acetate (PGMEA), OSHA 53; ethanol, NIOSH 1400; ethyl acetate, NIOSH S49. Errors associated with those measurements were estimated to be ± 15 percent at a 2σ confidence level.

Worker exposures were presented in terms of time-weighted average mixture TLVs, calculated according to ACGIH recommendations.⁽¹⁾ This choice was not meant to imply endorsement of one unit of permissible exposure versus another. The PGMEA did not have an established TLV, although its health effects were well documented and it had an AIHA Workplace Environmental Exposure Level Guide (WEEL) of 100 ppm.⁽²⁾ That WEEL value was used in this study as if it was a TLV.

All of the vapor components measured were primarily classified as irritants except for cyclohexanone.⁽³⁾ It was included in the mixture TLV for initial worker exposures (Figure 3) but was primarily a central nervous system depressant and secondarily an irritant. Initial worker exposures can be seen in Figure 3.

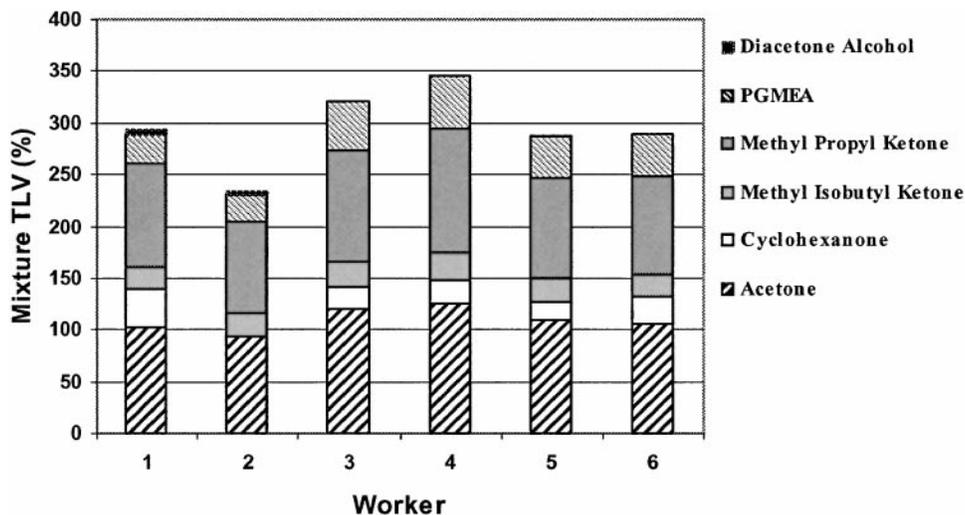


FIGURE 3
Initial worker exposures.

Characterizing Sources of Vapor Emissions

Release of Solvent Vapors from Printer Unit and from Ink on Printed Vinyl

Many of the measurements were accomplished using a field-deployable gas chromatograph/mass spectrometer (GC/MS). The NIOSH-developed instrument duplicated the capabilities of many laboratory GC/MS units, with additional capabilities to conduct real-time measurements by direct introduction of samples into the MS analyzer via a membrane separator.⁽⁴⁾ The instrument was useful in the workplace setting and in the laboratory to study the evaporation of solvent components from the printing process, and to evaluate process control measures. It also allowed quick on-site determination of constituents of complex mixtures of vapors and gases, using direct injection GC/MS. It could also avoid sampling tube "problems" for certain analytes such as propylene glycol monomethyl ether acetate (PGMEA), where the analyte can decompose on the sampling media.

Constituent chemicals could often be identified by measuring retention times of peaks in the total ion chromatogram and the ion spectra under a given retention peak. Once constituents were identified, non-interfering ions could be selected as characteristic for each component. That allowed measurement of real-time concentrations of specific component vapors in complex mixtures as a function of time and location in the workplace using selected ion monitoring and direct atmospheric sampling.

Quantification of solvent vapor concentrations was normally achieved through instrument calibration using standard concentrations in air of individual analytes (and reference clean air) and introducing them into the analyzer via whatever mode of measurement was being used. For long continuous measurements of individual analytes via selected ion monitoring, calibration concentrations were preferably introduced at the beginning and end of a run. Errors associated with the selected ion real-time measurements were estimated to be ± 10 percent (2σ) with $< \pm 5$ percent bias (error in standard concentration used for calibration).⁽⁴⁾ Several concentrations of an analyte were used to check detector nonlinearity (less than $\pm 5\%$ in this study). Figure 4 shows the GC/MS on the printing room floor, with the sample inlet line exiting the right inset panel and the computer on top.

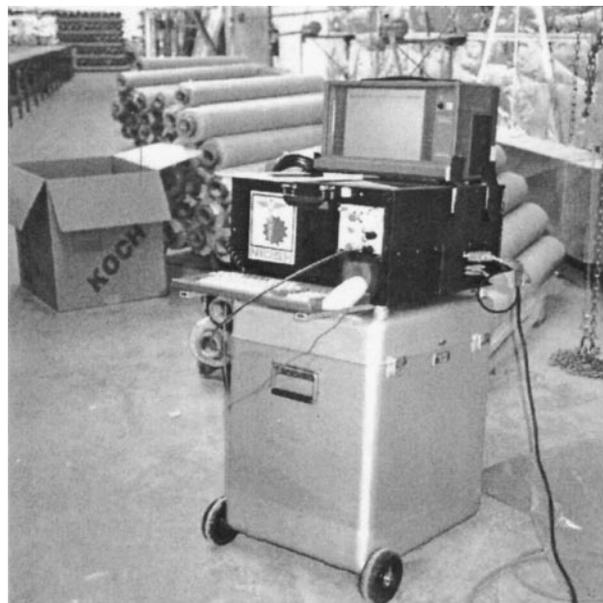


FIGURE 4

Portable GC/MS in use in printing facility.

In initial studies, the GC/MS was used to produce real-time simultaneous measurements of the concentrations of the three principal solvents used for diluting the ink; acetone, methyl propyl ketone (MPK), and PGMEA (see mixture A, Table I). The real-time simultaneous monitoring of the components of this particular solvent mix was complicated by the fact that the principal identifying ions for acetone (43 and 58 atomic mass units [amu]) were present in the other two components. Those components had ions unique to them (86 amu for MPK and 72 amu for PGMEA). Consequently, the acetone component could be determined by running separate standards for the three components and establishing a ratio for the 86 and 72 amu ions to the 43 or 58 amu ion for MPK and PGMEA. Thus, using the selected ion monitoring mode for the 43 (or 58), 72, and 86 amu ions, the contribution to the 43 or 58 amu ion signal from the MPK and PGMEA was first calculated and then subtracted from the 43 or 58 amu total, leaving the remaining 43 or 58 amu ion

TABLE I
Components of ink-thinning solvent mixes

	TLV (PPM)	% (by mass) Mixture A	% (by mass) Mixture B	% (by mass) Mixture C	% (by mass) Mixture D
Acetone	750	55	37		
Butyl Acetate	150				21
Ethanol	1000		10–20		
Ethyl Acetate	400		20–30		
MPK	200	35			
Methanol	200		1		
PGMEA	100 (WEEL)	10	20–30	94	63
DPM	100			6	16

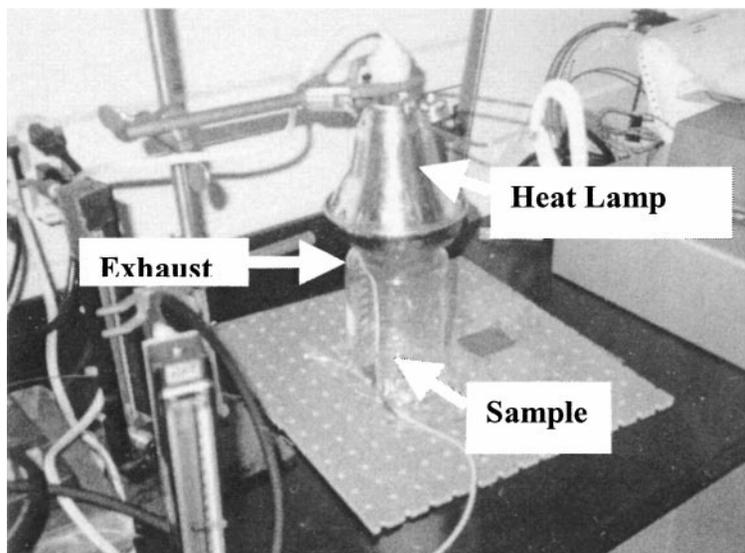


FIGURE 5

Test apparatus for observing vapor emissions from ink on vinyl sample.

signal due to acetone. The processing to determine the acetone component was done after gathering the data.

Some laboratory measurements were made to better observe the release of low volatility components from printed vinyl. An approximately 2" × 2" piece of vinyl with printing ink on one side (ink diluted with solvent ready for printing) was placed under a glass beaker with approximately 3.5 L/min air flow through the beaker. The GC/MS sample probe was taken off of a side stream of the exhaust air taken near the inside top of the beaker. The test apparatus is shown in Figure 5.

The sample was heated with an infrared heat lamp to approximately 40°C (measured by a thermocouple probe contacting the back of the vinyl sample) to accelerate the release rate of the slower evaporating solvent components, as it was difficult to see the release of PGMEA in initial measurements without added heat. Figure 6 shows the change in the concentrations and ratio of concentration of the three solvent components as a function of time for released vapors. The lower graph shows the same PGMEA concentration curve as in the upper graph, with increased gain.

To estimate the solvent content in the ink, we placed a sample of ink film, similar to that on the vinyl sample, on a Mylar film and heated the sample to approximately 90°C. After 3 h there was a 71 percent loss in mass, and at 48 h, a 76.5 percent loss. The results of this study can be compared to what was measured with printed ink on vinyl in the printing facility. Figure 7 shows the concentration of the three solvents as a function of time, with the GC/MS sampling probe near a print on the printing table during printing. The large peaks indicate the passage of a printer unit.

Contributions of Emissions from Printer Unit and from Printed Vinyl

We estimated the fraction of total solvent emissions from evaporation off of the printer unit (from the ink/solvent mixture

on the printing screen) as well as that coming off of the deposited ink/solvent on the vinyl, by measuring the concentration of solvent vapors in the workroom air during two printing runs. Measurements were first made of emissions resulting only from solvent evaporation from the top of the printer unit, by using a closed printing screen that allowed no ink/solvent to be deposited on the vinyl. Measurements were then made using a 305 mesh count printing screen having a 2 ft × 2 ft open area

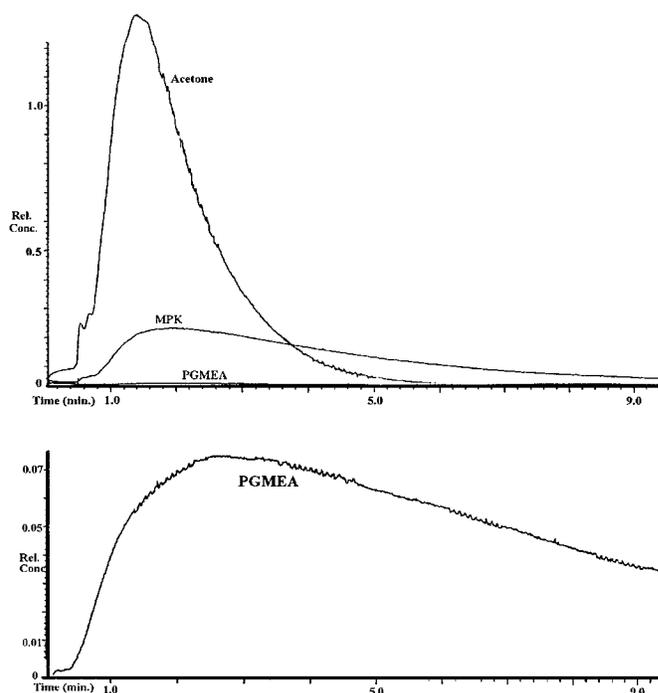


FIGURE 6

Vapor emissions from ink on vinyl sample.

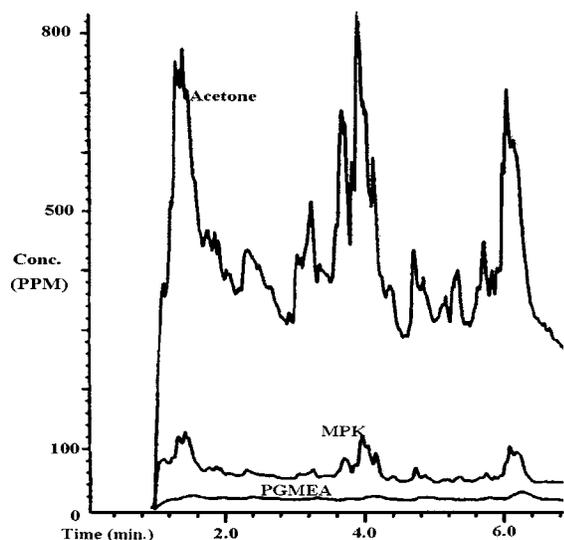


FIGURE 7

Vapor concentrations near print on printing table.

(similar to typical printing screen), with emissions coming from the printer top and printed area. The open area screen and prints are shown in Figure 8. Printing runs were made with the original ink/solvent mix (thinning solvent A, Table I).

Equal numbers of print-producing operations were accomplished in both printing runs. Before each run, the solvent vapors were purged from the workroom to levels near background. All sources of outside air and exhaust were shut off, and solvent vapors were allowed to build up in the room during the run. Air recirculation in the room was retained to enhance mixing of the solvent vapors in the room. This resulted in a concentration of solvent vapors in the workroom air directly proportional to the quantities of solvent vaporized. Due to the short time intervals



FIGURE 8

2 × 2 ft printed areas on table and associated printing screen.

TABLE II

Measurements for determining printer unit vapor emissions contributions

	PGMEA	MPK	Acetone
Concentration using blank screen (ppm)	6.4	98	290
Concentration using open area screen (ppm)	12.5	136	442
Contribution from top of printing unit (%)	51	72	66

for the runs, air concentrations during these tests did not exceed those normally experienced during production runs.

The contributions of the three principal solvent mix components (PGMEA, MPK, and acetone) were measured using methods similar to those described previously. Concentration values resulting from the first run were subtracted from those of the second run at equal times from the start of each run. This yielded solvent vapor concentrations from evaporation from the printer unit top only, and from the deposited ink on the vinyl (with minor amounts from the bottom of the printing screen). Results are shown in Table II.

Exposure Reduction

Personnel Protection

As mentioned in the introduction, solvent vapor concentrations existing at the time our study began had prompted the company to require workers in the print room to wear half-face air purifying respirators with organic vapor cartridges. Cartridges were replaced daily and workers had annual health exams.

In a later OBWC review of that program, NIOSH recommendations regarding respirator use were used as guidance.⁽⁵⁾ OBWC advised the company that respirators only be used when engineering controls were not feasible or effective, while controls were being installed or repaired, or for emergency or intermittent situations. Full-time, long-term use of respirators seldom constitutes a satisfactory means of controlling employee exposure. Assuring continuous proper fit and function of respirators as well as worker compliance with the program would often be problematic even where full-time industrial hygiene oversight existed. Worker stress was high due to the substantial physical effort involved in printing and was difficult to justify except where no viable alternatives existed. Respirator use was considered a temporary measure allowing production to continue while other solutions to the problem were developed and implemented.

The initial workplace concentrations slightly exceeded the 1000 parts per million (ppm) maximum use concentration for air-purifying elements in respirators; however, those levels were lowered to less than 1000 ppm shortly after this study began. The company estimated costs for the program as approximately \$15,000/year for respirator cartridges and \$500/year for physicals.

Ink-Thinning Solvent Substitution

Using a different ink-thinning solvent mixture to lower worker exposures was considered attractive, as this possibly would not involve any significant capital investment or changes to a well-functioning printing process developed over many years of operation. When testing an ink-thinning solvent mixture used with a particular ink, the company considered the following; (a) the compatibility of the solvent with the ink used and its behavior in the printing process, (b) the ability of the printed product to adhere well to the vinyl after a test sample was washed in a washing machine, (c) the amount of solvent required to perform a certain amount of printing, (d) the cost and availability of the solvent, and (e) the ability of the solvent to lower worker exposures to a level allowing workers to not have to wear respirators. Several of the components of solvent mixtures A and B were very volatile and flammable. The somewhat uncontrolled methods of handling these solvents were alarming and it was clearly desirable to move to solvents having lower flammability properties, and preferably with lower National Fire Protection Association (NFPA) flammability hazard indices.

Other solvent-related problems included difficulties with printing under conditions of high humidity. It appeared that water collected on the printing screen and caused problems in printing. It seemed likely that absorption of water vapor by the solvent could promote that problem. Local cooling of the printing screen through evaporation of the solvent could also lead to condensation of water vapor on the screen. It appeared likely that the use of lower vapor pressure solvents could reduce local cooling of the screen. The high relative evaporation rates, hygroscopic properties, and flammability of acetone in mixture A, Table I, made it particularly desirable to eliminate.

The principal components of the ink-thinning solvent used at the beginning of this study (see mixture A, Table I) had established time-weighted average TLVs that were quite high; 750 ppm for acetone and 200 ppm for MPK. Minor components included diacetone alcohol, methyl isobutyl ketone, and cyclohexanone with TLVs of 50, 50, and 25 ppm, respectively. Company officials indicated that the choice of the existing ink-thinning solvent was made prior to their involvement, and it was not clear what part the various components played in its function or if it was optimal for their process. A local solvent vendor used by the facility suggested a different ink-thinning solvent mix, expecting that a lower personnel exposure might result. The new solvent consisted of the components in Table I, mixture B. They had chosen component solvents having higher average TLVs; however, mixture B still contained acetone and other very volatile and flammable components.

Trial of European Ink/Solvent System

An interesting example of the trial of a substitute ink/solvent system was one where a European company offered what initially appeared to be a suitable ink/solvent substitute. They claimed to have “environmentally friendly” inks and solvents that would work in the company’s vinyl printing operation. Al-

though the vendor claimed that their solvent met the highest standards of safety, little or no toxicity data was available for several of the solvent’s components. We pointed out that there was limited toxicological information on the solvent/ink system and cautioned the company relative to its use. Without established TLVs or equivalent safety documentation, there was no way to ascertain whether the product was safe to use or environmentally friendly. The company decided to purchase that solvent/ink system. In the first full production run, employees complained of severe throat irritation and burning eyes, and there were problems with the ink’s adhesion. Its use was discontinued. We pointed out that they were fortunate to have such clear acute symptoms occur, as it could also have been possible that no immediate symptoms would be obvious, yet long-term detrimental health effects could exist.

Reducing Solvent Use by Substituting a Finer Printing Screen Mesh

The European ink/solvent system vendor indicated that the pigments used in their inks had a finer particle size than the inks the printing company was currently using. That allowed the use of a finer printing screen mesh size, resulting in less solvent and ink use and lower amounts of solvent vapor. The mesh count is the number of threads per inch in the screen material and is directly related to the size of the pores and percent open area of the screen (also dependent on the thread diameter and weave).

Using this information and the thickness of the screen, a “theoretical ink volume” is derived, which is an index of the amount of ink that is expected to be deposited on the vinyl film. The company switched from 156 to 305 mesh count screens during the production run using the European solvent/ink system, resulting in a reduction in the theoretical ink volume from approximately 35 to 17 relative units (51%).⁽⁶⁾ They tried their current solvent/ink with the finer mesh screen and found that it worked well, reducing their solvent/ink use by 35–40 percent. In some cases the use of less ink resulted in an insufficient image density; however, that problem did not appear to be common and could be solved for specific cases.

Measurements of Personnel Exposures After Process Changes

After changing the mesh count of the screens and using the ink-thinning solvent B, OBWC again measured worker exposures. The results are shown in Figure 9.

Enclosing the Printer Units

The studies of solvent vapor emissions from the printer unit versus the printed material indicated that substantial reductions in emissions could be achieved by better controlling the release of vapors from the printer unit (see Table II). It was also clear that this was quite dependent on the relative evaporation rates of the component solvents used and their proportions in the solvent

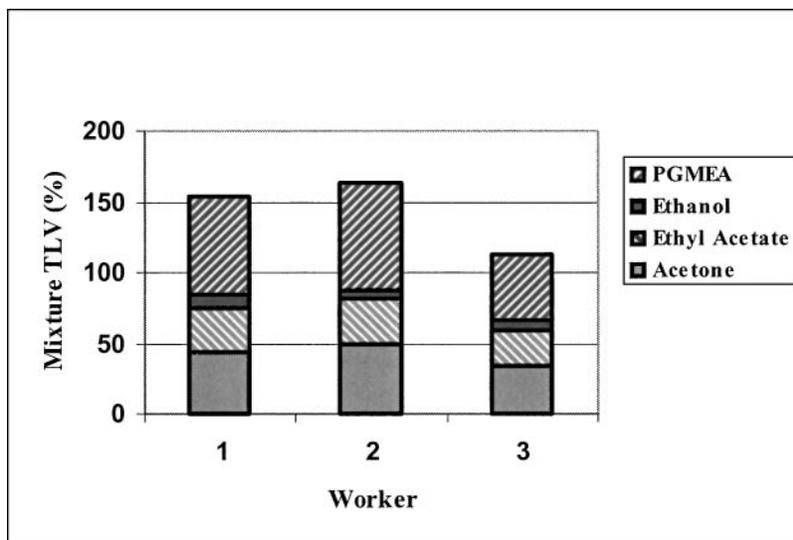


FIGURE 9
Worker exposures after initial process changes.

mix. Solvent mixes having large quantities of highly volatile solvents, such as acetone and MPK, would benefit the most from printer enclosure. It appeared that if the printer unit could be enclosed, solvent evaporation could be substantially reduced due to the establishment of a near equilibrium condition of vapor concentration over the ink/solvent matrix. Consequently, we investigated the feasibility of constructing an enclosure that could:

- provide adequate visibility of the printing screen for the printer operator
- provide easy access to the printing screen for the printer operator to add solvents to the ink, correct problems on the screen surface, and meet other operational needs
- include light-weight construction for use with the existing printer carriage mechanism
- be constructed with materials compatible with the solvents used
- provide adequate sealing around the printer and the movable printer squeegee arm, without interfering with the motion of the arm

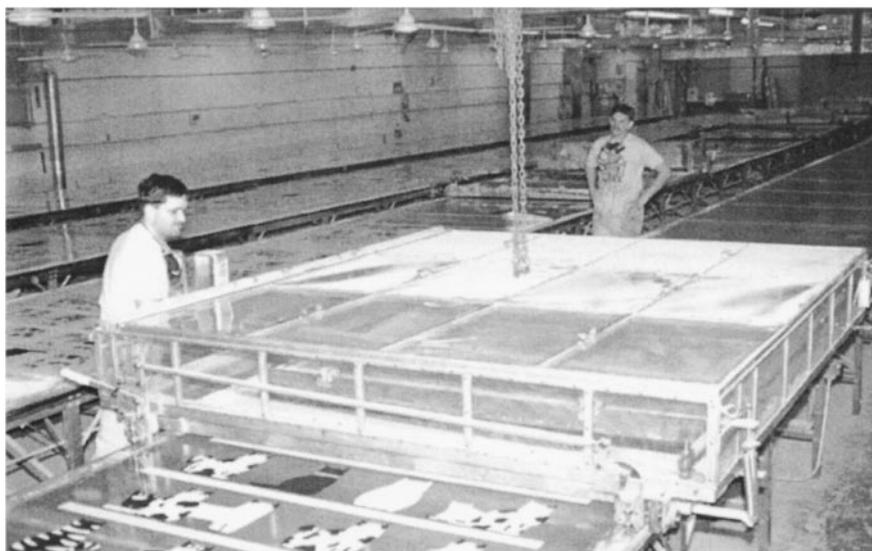
It appeared that an enclosure could have advantages beyond that of reducing vapor emissions, including reducing the time required for screen maintenance due to the drying of ink on the printing screen, and less solvent replacement resulting from reduced solvent consumption. It would also reduce the access of water vapors to the printing screen, ink, and solvent, reducing the undesirable effects of moisture on the printing screen.

It was possible that a reduction in exposures to the operator of the printer could be partially due to lowered local concentrations of solvent vapors next to the enclosed printer units. The printer enclosure design consisted of an aluminum framework over the printer unit, with hinged side panels allowing for easy

access to the printing screen from all sides. The transparent top, consisting of two panels having a 0.25-mm (0.010 in)-thick Mylar film supported on a lightweight aluminum frame, allowed the printer operator to monitor the printing operation visually. The two top panels together weighed approximately 17 lb and were supported by a 1 in recess in the top of the enclosure frame. Each panel could be quickly lifted off of the frame using handles attached to it, allowing easy access to the printing screen for cleaning and screen changing.

Providing a seal for the enclosure in the area that the printer squeegee-operating bar penetrated it was particularly difficult. This was accomplished using a “U” shape in the printer arm that jogged over the outer vertical edge of the enclosure. A flexible silicone rubber overlapping seal was used along the top edge of the enclosure where the arm slot penetrated the enclosure. The rubber was very flexible, yet retained its shape well due to a fiberglass fabric reinforcement. The seal was designed to follow the natural movement of the squeegee arm during the printing process.

Two tests of the effectiveness of such units were conducted. The first was done using the original ink/solvent system, mixture B, and was accomplished by monitoring thinning solvent usage during production runs with the printer enclosure top on and off. That showed a reduction in ink-thinning solvent added during production by approximately 35 percent, a 26 percent reduction in total mixture B solvent usage, and an 18 percent reduction in total solvent usage (solvents in ink base [approximately 77% low-volatility solvents], original thinning of ink, plus solvent added during production). The second test included GC/MS measurements made during a production run with and without the printer enclosure covers, using the new ink/solvent system with mixture D. The results of those measurements are shown later in Figures 12 and 13.

**FIGURE 10**

New printer unit with printer enclosure.

Those measurements convinced the maintenance engineer of the merits of redesigning the printer units to incorporate such an enclosure. Due to the need for improvements in the existing printer units and their worn-out condition, it was decided to build all-new printer units (see Figure 10). The new printer units incorporated changes to improve print registration, which was important for printing using the four-color process (using very small dots of primary colors and black to form a color image).

Other Control Methods Considered

We also examined other possibilities for controlling vapor emissions or removing vapors from the workplace air. These included alternate printing methods, local ventilation (push-pull ventilation and ventilation over the printer units), and cleaning the workplace air.

Various process changes were investigated including the possibility of converting to a stationary offset or printing screen printing process whereby the vinyl was moved through a stationary printing apparatus. This would allow the application of a very localized and economical ventilation system for the printer unit. While technology exists for offset or rotary screen printing on vinyl, due to the sizes of the images to be produced the equipment involved would be very large and appeared to require a prohibitive capital investment.

Changing the present screen printing method to one using stationary printer units with the vinyl moving appeared to present substantial problems in "registration" and distortion of the vinyl between printing stations. While the company had not eliminated this as a possibility, it did not appear to be a realistic goal at that time. The company claimed that the existing printing system allowed them extreme flexibility in the type of images that could be printed, as well as very low setup costs for changing images.

This allowed them to remain economically competitive with domestic and overseas competition.

A push-pull industrial ventilation system, as described in the ACGIH Ventilation Handbook,⁽⁷⁾ was considered. Considering that the printer units move continuously along the printing tables laying down an ink/solvent mixture onto a vinyl sheet, and assuming a 7 ft × 150 ft print area and four printing tables in use, the surface area of the vinyl receiving the ink/solvent mixture would be 4200 ft². Assuming that practical push-pull ventilation could be installed to capture emissions and using a design exhaust flow rate of 75 cfm per ft² of surface area, the total flow rate required for the system would be approximately 315,000 cubic feet per minute (cfm). Not only would such a system be expensive to install and operate, but it would greatly exceed the capacity of the current air incinerator. It was also considered to be incompatible with the existing printing equipment.

We investigated the possibility of controlling emissions from the printer units by using a canopy type of local exhaust hood that was an integral part of the printing unit. The exhaust connection of the canopy would connect into a zipper duct located above or adjacent to the printing table by being inserted into a dynamic (or "zipper") seal on the duct. The nature of such a duct seal would allow a moving duct connected to the printer unit to be inserted into the sealed duct during travel of the printer unit along the direction of the sealed duct. An initial appraisal of such an approach was discouraging, in that it appeared very difficult to design the exhaust connection such that it would not restrict access to the printing screen from around the periphery of the printing apparatus or to avoid introducing mechanical stresses on the printer unit that could interfere with its operation. Extremely easy access to all portions of the printing apparatus was essential to the efficient use of the printer. Additionally, local exhaust over the printing screen

appeared likely to increase the solvent evaporation rate from ink on the printing screen, presenting several problems, including increased solvent use, local drying of the printing screen, and condensation of water vapor on the screen. Also, our study of the portion of solvent vapors released from the top of the printer unit indicated limited usefulness from this method (see Table II).

The removal of solvent vapors from the air of the printing room by various air-cleaning methods was considered. Such methods normally depend on the sorption of the vapors on a sorbent such as activated carbon or molecular sieve materials. The possible benefits included reduced costs of heating and cooling energy and the possibility of using existing ink/solvent systems while reducing workplace exposure levels to target goals of 25–35 percent mixture TLVs. Some systems also allowed the recovery of solvents for reuse or disposal; however, such recovery equipment was very expensive.

A general consideration for any such method would be that all air in the workroom would have to be cleaned by being processed through the sorbent media by some means and returned to the workroom. The efficiency of removal (EOR) (%/100) would determine the required rate of air recirculation. In order to achieve the removal rate resulting from 16,000 cfm of dilution ventilation (factor of 4 reduction in workroom concentrations), a recirculation ventilation rate = 16,000/EOR would be required. To accomplish this, a ventilation arrangement similar to that for single-pass ventilation would be required, with the air inlet to the recirculating blowers at the point of discharge from the facility.

A major difference in these setups would be the need to have high-efficiency particulate filtration before the sorbent beds to avoid loading of the beds with small particulates, and higher system flow rates. Such filters normally have significant pressure drops across them, leading to much higher energy consumption for air circulation and high maintenance costs. In addition, the 200 ft return air ducts also create an added pressure drop and capital investment.

We obtained some estimates of cost for representative air-cleaning equipment from equipment vendors. The estimates were for equipment only, less installation costs. One commercially available system used a large rotary sorbent bed with room air flow to part of the bed area, and a hot air desorption flow to another part of the bed with concentration ratios of approximately 6–20:1, depending on solvent vapors and equipment design. Concentration ratios of 10:1 appeared very feasible. In typical installations, the desorption air stream with concentrated solvent vapors would be sent to a catalytic oxidizer.

A combined preconcentrator and catalytic oxidizer for a 20,000 cfm flow rate was estimated to cost \$550,000. The energy use rate for preconcentrator fans would be approximately 20 kW due to the high pressure drop across the bed.⁽⁸⁾ However, natural gas operating costs would be much less than a conventional catalytic oxidizer due to the much lower flow rate and the substantially increased concentration of solvent vapors

providing fuel. State-of-the-art catalytic oxidizers also utilized heat recovery to further reduce fuel costs. A major advantage of air cleaning was that it was likely to be usable with conventional ink/solvent systems. Smaller HVAC capacities than that for single-pass ventilation (without energy recovery) would be needed and overall energy use was likely to be smaller.

Disadvantages of sorption air cleaning included a high capital investment cost, complex equipment requiring well-trained operating personnel, the possible need for disposing of or recycling used sorbents, and the need for real-time monitoring of system performance to assure that system efficiencies remain acceptable for each solvent vapor present. It was also possible that a system design might not be compatible with solvent components when ink formulations changed. Ink vendors did not specify exact contents of their inks or guarantee that they would stay the same.

Development of New Ink/Solvent System and Improved Ventilation

Basis for OEPA Restrictions on Solvent Vapor Emissions

Emissions resulting from the prints drying on the production room tables and evaporation from the bottom of the printing screen (a minor source) were still uncontrolled. A study of options indicated that control of this was not practical with the existing process. It seemed that increasing dilution ventilation rates was the most direct and dependable solution. However, increasing the size of the catalytic oxidizer appeared cost prohibitive. Consequently, we examined how the OEPA requirements for the catalytic oxidizer might be avoided. As the existing workplace conditions were the result of attempting to meet the OEPA requirement for discharge of solvent vapors to the environs, a detailed review of OEPA regulations⁽⁹⁾ was conducted to better understand what changes to the plant's ink/solvent system would most benefit the workplace air quality.

We found that the major problem was that "photochemically reactive" materials, as defined by the OEPA, were contained as solvents in the inks. Their definition was as follows: 'Photochemically reactive material' means any liquid organic material with an aggregate of more than twenty percent of its total volume composed of the chemical compounds classified below or which exceed any of the following individual percentage composition limitations, referred to the total volume of liquid:

- a) a combination of hydrocarbons, alcohols, aldehydes, esters, ethers or ketones having an olefinic or cyclo-olefinic type of unsaturation: five percent;
- b) a combination of aromatic hydrocarbons with eight or more carbon atoms to the molecule except ethylbenzene: eight percent;
- c) a combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene or toluene: twenty percent."

The ink-thinning solvents the company was using were not included in that definition; however, the aromatic solvent content of the inks was. Solvents outside of that definition did not have emission quantity limitations assigned to them. We contacted the ink manufacturer the company was currently using, as well as most other manufacturers of vinyl printing inks listed in the Thomas Register.⁽¹⁰⁾ Their present manufacturer suggested a few of their other products to try. Component solvents used in those inks included several with low TLVs, and trial printings with those inks were not satisfactory. No other ink manufacturers had inks they could recommend, and most said they did not think satisfactory inks could be produced without the use of photochemically reactive solvents.

To use the present inks in the quantities needed, the company had to use control equipment to meet a 40 lb/d limit in the OEPA regulations. A catalytic oxidizer and negative pressure in the process area were required for complying with those emissions limits, and meeting "best available technology" (BAT) requirements in PTI 14-3434. The review of regulations indicated that changing the ink/solvent system to one having no photochemically reactive components was a possible fix. That could allow elimination of the requirement for the catalytic oxidizer and substantial increases in dilution ventilation for the facility. However, the company also needed to meet BAT requirements, whereby they could be required to reduce emissions if it were feasible to achieve at a cost of up to \$7000/ton of solvent emissions eliminated per year.

NIOSH and OBWC representatives met with OEPA representatives to review applicable OEPA regulations and possible options for a cost-effective approach to reducing personnel exposures to solvent vapors. It appeared that elimination of photochemically reactive solvents was a key to securing an OEPA permit allowing improved ventilation in the facility. The company supplied us with annual operating cost data for the use of the present catalytic oxidizer of \$65,700/year, not including costs related to employee retention factors (it was difficult to hire and keep people with mandatory respirator use) and long-term maintenance expenses (replacement of catalytic element). However, the existing catalytic oxidizer did not constitute a viable long-term option, considering employee protection.

In 1996, the company received cost estimates of \$500,000 for a catalytic oxidizer of the size required for air flows four times those currently existing. Annual costs for such a unit were estimated to be \$150,000 for leasing of equipment, \$75,000 energy costs, and \$25,000 maintenance costs, or a total of \$250,000/year. That would be approximately \$8300/ton of emissions controlled. In addition, a new HVAC system with a flow rate equal to the new catalytic oxidizer would be required, with additional capital and operating expenses. It was argued that since emissions would not be photochemically reactive, those costs would exceed those requiring further emissions reductions associated with BAT. Instead, printer enclosures were likely to technically and economically satisfy BAT requirements.

Developing a New Ink/Solvent System

Removing photochemically reactive components from the inks appeared necessary before unrestricted dilution ventilation for the workplace could take place; consequently, we proceeded to explore substitute ink-thinning solvents and the development of alternate ink formulations. A review of literature produced little useful information on desirable ink formulations,^(11,12) and we were advised that most ink formulation information was protected by the industry as trade secrets.

We conducted a survey of component solvents that could possibly reduce solvent usage and personnel exposure while being compatible with the existing printing process. The overall choice of a solvent mixture involved a somewhat complex balancing of many factors, including component solvent toxicities as reflected in TLVs, relative evaporation rates (RERs), flammability, cost, availability, etc. Important factors for which data were not immediately available included an ability to dissolve polyvinyl chloride (believed to be related to good adhesion of ink to vinyl), odor, and its behavior in the overall printing process with existing inks, including quality of the printed image, printing screen plugging, and sticking and dissolving of the printing screen.

It was desirable to minimize evaporation of solvent before the ink was placed on the vinyl while having sufficient volatility for the ink to dry in an acceptable time interval between the printing of successive colors. The solvent should efficiently reduce the viscosity of the ink for effective penetration of the printing screen by the ink/solvent mixture, but the ink spot must not spread or bleed after printing. Most of these factors had to be evaluated experimentally.

A tabulation of candidate solvents shown in Table III was developed by selecting solvents having a TLV or WEEL equal to or greater than 100 ppm, relative evaporation rates (rate of evaporation compared to butyl acetate [butyl acetate = 100]) under 300, and NFPA flammability ratings of 3 or lower.⁽¹⁻³⁾ Flash point temperatures for the candidates were also included to help judge ignition potential for the materials (preferably above room temperature). A few solvents used in solvent mixes A and B, but not meeting those criteria, were also included. Several solvents having TLVs of 100 or larger did not have data available on RERs. In nearly all such cases the solvent was not in widespread industrial use and was eliminated from the table based on cost/availability.

We tried using only MPK as the ink-thinning solvent since it was a principal constituent of the existing solvent, was much less volatile than other major components, and we hoped it would substantially reduce solvent use and worker exposures. Three test printings with MPK as the only added solvent indicated that the total solvent use was approximately 53 percent that of the regular solvent. Unfortunately, it was found that using MPK had some problems that couldn't be overcome, included sticking of the screen to the vinyl and clogging of the pores in the screen. Tests of some other solvents were similarly unsuccessful.

TABLE III
Candidate component solvents for use with vinyl printing inks

Compound	CAS	TLV	RER (Butyl acetate = 100)	Fire rating	Flash point (°C)
Acetone	67-64-1	750	560	3	-9
n-Amyl acetate	628-63-7	100 (50)	42	3	25
sec-Amyl acetate	626-38-0	125 (50)	90	3	32
2-Butyl acetate	111-76-2	200	200	3	16.7
n-Butyl acetate	123-86-4	150	100	3	22
sec-Butyl alcohol	78-92-2	100	130	3	24
tert-Butyl alcohol	75-65-0	100	NA	3	11
1,2-Dichlorethylene	540-59-0	200	NA	3	21
Diethyl ketone	96-22-0	200	NA	3	13
Dipropylene glycol monomethyl ether (DPM)	34590-94-8	100	2	2	86
Ethanol	64-17-5	1000	240	3	13
Ethyl acetate	141-78-6	400	620	3	-4.4
Isoamyl acetate	123-92-2	100	42	3	25
Isoamyl alcohol	123-51-3	100	19	2	43
Isobutyl acetate	110-19-0	150	150	3	18
Isopropyl alcohol	67-63-0	400	230	3	12
Methylal	109-87-5	1000	88	3	-26
Methyl ethyl ketone	78-93-3	200	32	3	-9
Methyl propyl ketone (MPK)	107-87-9	200	230	3	7
n-Propyl acetate	109-60-4	200	71	3	13
n-Propyl alcohol	71-23-8	200	130	3	15
Propylene glycol monomethyl ether	107-98-2	100	0.02	2	32
Propylene glycol monomethyl ether acetate (PGMEA)	108-65-6	100	34	2	42

Initial exploration of new ink formulations included contacting manufacturers of the plastic resins used in vinyl inks. One manufacturer, DuPont Chemical, had personnel with experience in use of their plastic resins in ink applications. We were given some suggestions on a formulation, based on past ones used in other types of printing.⁽¹³⁾ It was recommended that a mixture of vinyl resin with acrylic resin be used. The solvents used in that formulation were cyclohexanone and "Aromatic 100," which were, unfortunately, photochemically reactive. Some other solvents were suggested as possible substitutes, including acetone, butyl acetate, diacetone alcohol, methyl amyl ketone, and 'methyl PROPASOL acetate'. A few of those solvents were not photochemically reactive and were included in our list of candidate solvents in Table III.

After further review, only a few solvents met the goal for low flammability (preferably NFPA flammability of 2 or less), TLV \geq 100, RER <300, had the ability to dissolve adequate quantities of the vinyl and acrylic resins, and were readily available industrial solvents with prices similar to those in mixtures A and B. The resins used were Union Carbide Solution Vinyl

Acetate-Vinyl Chloride Copolymer Resin VYNS-3 and Rohm and Haas Acrylic Resin A-11 (powder). One was a copolymer of vinyl acetate and vinyl chloride, which gave body and pliability to the ink as well as an ability to solvent weld to the surface of the vinyl film. The other was an acrylic resin to block the migration of plasticizers from the vinyl film to the ink, which caused discoloration. The Organic Pigments used were Sun Chemical Co. Sunfast Pigments. Inorganic Pigments were Chevron Chemical Co. Acetylene Black and DuPont Chemicals TiO₂ (Ti-Pure TiO₂).

As a starting point in these experiments the selection of the various solvents, resins, and pigments seemed to be based on logical choices. However, it soon became clear that the very complex interactions of the many important factors in the ink/solvent system were only sorted out by much experimentation with various formulations. These factors included molecular interactions between solvents, resins and pigments in the mix, wetting effects on the vinyl surface and the printing screens (related to screen clogging), the solubilizing properties of the solvent mix, evaporation rates, and the effect of the mixture on the behavior

TABLE IV
Ingredients to produce 1 gal (3.8 L) of NIOSH-developed vinyl printing ink

	DPM (gal)	PGMEA (gal)	Butyl acetate (gal)	VYNS-3 lb	A-11 lb	Pigment lb
White ink	0.042	0.70		0.53	0.328	1.75 TiO ₂
Black ink	0.064	0.79		0.50	0.25	0.45 Acetylene black
Organic pigment ink	0.12	0.50	0.19	0.50	0.25	1–1.5 Organic

of the pigments. A comprehensive description of the complexity of solvent, solute, and particulate interactions can be found in the literature.⁽¹⁴⁾

Initial printing attempts using PGMEA as the solvent with ink mixes using inorganic pigments had problems with screen sticking and clogging. After much experimentation, it was found that adding DPM corrected that problem. We found that the organic pigments did not behave the same as inorganic ones. We finally got ink using organic pigments to perform satisfactorily by adding butyl acetate to the mix.

PGMEA and DPM had low flammability ratings (NFPA category 2). Butyl acetate had an NFPA flammability rating of 3, probably due to a slightly lower flash point temperature (see Table III). However, it was substantially less flammable than acetone or ethyl acetate in mixture B, Table I.

We were fortunate that Sun Chemical Corporation, the largest producer of organic pigments for the paint and ink industry, was located nearby. They gave us some technical advice on the selection of pigments and numerous samples for experimentation. They have an extensive listing of color pigments and their compatibility with various solvents, including those suitable for the

four-color process. Pigments that dissolved in the solvents we used had to be avoided. While all the pigments used had a “nuisance dust” hazard rating, tiny amounts of the organic pigments could cause a mess. Experience in mixing inks showed the need to handle pigments in a glove-box like enclosure. To address that problem, we designed a multi-station ink production area, with enclosed and ventilated stations for weighing and adding pigment to the mix.

Our studies resulted in a new ink formulation using two or three solvent components, two resin components, and pigments necessary to reproduce the colors needed (see Table IV). In the new ink system the same solvent mixture was used for making and thinning the ink, and the ink was mixed ready to print (saving a pre-mixing step with the previous ink). The inks were mixed by first mixing the solvents and resins as a clear mix. That clear mix was then blended with the pigments for 24 h in a ball mill, using 1" steel balls. The ball mills can be seen against the wall in Figure 11. Plastic ball mill barrels can be seen on the ball mill rotational mechanism on the benches and also sitting on the floor. The ball mill containers could hold up to 4 gal of ink mix, and the containers were used to temporarily store mixed ink.

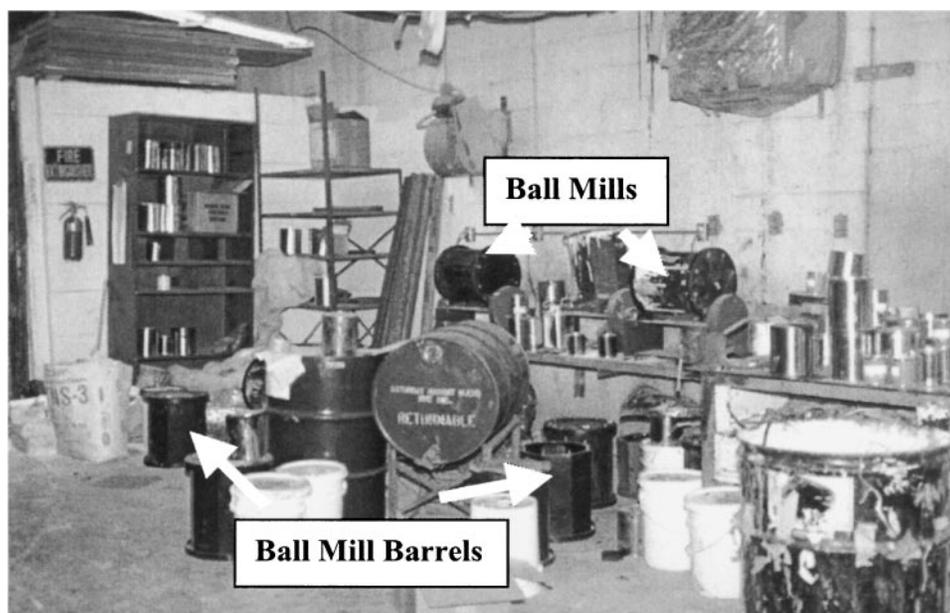


FIGURE 11
Ink mixing equipment.

Over an 18-month period, numerous test runs of the new ink took place. Several problems were identified and solved, as follows:

- Acetylene black was the only black pigment that seemed to work well with the new ink mix. However, it resulted in the printed ink being a very weak electrical conductor, which caused problems with radio-frequency arcing in the vinyl heat sealer. This was corrected by using insulated feed rollers in the heat sealer.
- When used with the four-color process, the new ink would form smudged dots with some colors. There were two causes for this. One was a process defect in the production of screens, which resulted in a somewhat porous emulsion on the exposed portions of the printing screen. The new ink was more sensitive to the defect than the previous ink. Also, it appeared that certain colors spread out on the vinyl surface after being deposited. We found that the addition of butyl acetate to the ink mix greatly reduced or eliminated this problem. The two corrections essentially eliminated the problem. The butyl acetate also eliminated slight tendencies for screen clogging or sticking and shortened the drying time.
- On certain rolls of vinyl (about one in fifteen), spots on the vinyl would be present that the ink did not adhere to well. These spots also caused some adhesion problems for their old ink, but to a lesser degree. We suspected that the spots were areas where there was excess plasticizer present. This could result from poor mixing of the plasticizer into the vinyl resin. The vinyl used was of the lowest grade available. The vinyl manufacturer was consulted. The vinyl manufacturer supplied two new batches of vinyl for further testing. One batch was of the same quality as the old stock, except an anti-blocking agent was added. The vendor mentioned that the additive caused the vinyl to roll up more evenly. It is not clear as to whether it had any properties that would help the “spot” problem. The higher-grade vinyl was made by another process and was a very clear even film. It is likely that producing a film of such clarity would require controlling all aspects of the process to the degree that inhomogeneous mixing of plasticizer would not be tolerated. A half-day test printing on the new high-quality vinyl took place with no problems observed. Further tests with the lower quality vinyl with the added blocking agent also proved successful, with no adhesion problems observed. That vinyl then became the standard material for further production.
- Certain red pigments caused a detectable “bleed” onto adjacent white colors when the curtain was washed in a washing machine. Most customers never wash a curtain, and would probably never notice the effect if

they did. This bleed was correctable by over-coating the red pigment with white or clear ink. In many designs this would mean re-doing the white screen to back-cover the red areas. In the few instances where that was not possible because of its appearance, a new screen could be made that would print clear ink over those areas. We tested both methods, and both worked well. The cost of over-coating with white is negligible, as white is used in nearly all images. Over-coating with clear would cost more, as it would add another step to the printing process, but it would be less than adding a color to a design since clear ink costs about one-fourth of average pigmented inks (most images use three to six separate colors). Finding alternate red pigments could also possibly reduce or eliminate the problem.

Measurements of Workplace Solvent Vapor Concentrations

Using Improved Inks and Ventilation

Vapor concentrations of organic solvents in the printing room were measured several times during printing operations while using the NIOSH developed inks. Those measurements were made with the catalytic oxidizer system operating, producing near homogeneous mixing of approximately 4000 cfm of clean makeup air with the workroom air. Measurements were also made with higher flow rates, using the catalytic oxidizer and other exhaust fans installed in the room, and with outside doors to the room open. That produced a fourfold increase in the total exhaust rate to approximately 16,000 cfm.

The first example was a production run that was somewhat atypical, in that the pattern used only one ink color; consequently, only one printer unit was used. However, the total area of the printed area was quite large (similar to those using multiple colors). This resulted in lower than normal concentrations of solvent in the workplace atmosphere. This run consisted of printing of 12 tables with the printer cover on and twelve with the printer cover off. It also included a change in ventilation rate after near-equilibrium conditions had been established, showing the ratio of concentrations for the two ventilation rates during production. GC/MS measurements of air concentrations for PGMEA are shown in Figure 12, and for butyl acetate in Figure 13. Both of these came simultaneously from the same GC/MS run, with ion monitoring for PGMEA (72 amu ion) and butyl acetate (56 amu ion). Contributions from DPM (103 amu ion) were negligible and are not shown.

Calibration of the system was accomplished using clean air at 44 min, 100 ppm butyl acetate at 45 min, and 100 ppm PGMEA at 46 min. Measurements of room air started after 6 tables of the 12 table production run (with the printer enclosure) had been completed. The ventilation rate was 4000 cfm from 0–23 min. At 23 min, when the first set of 12 tables was completed, the ventilation rate was increased to 16,000 cfm. At 78 min, after the room air had returned to pre-production concentrations, a

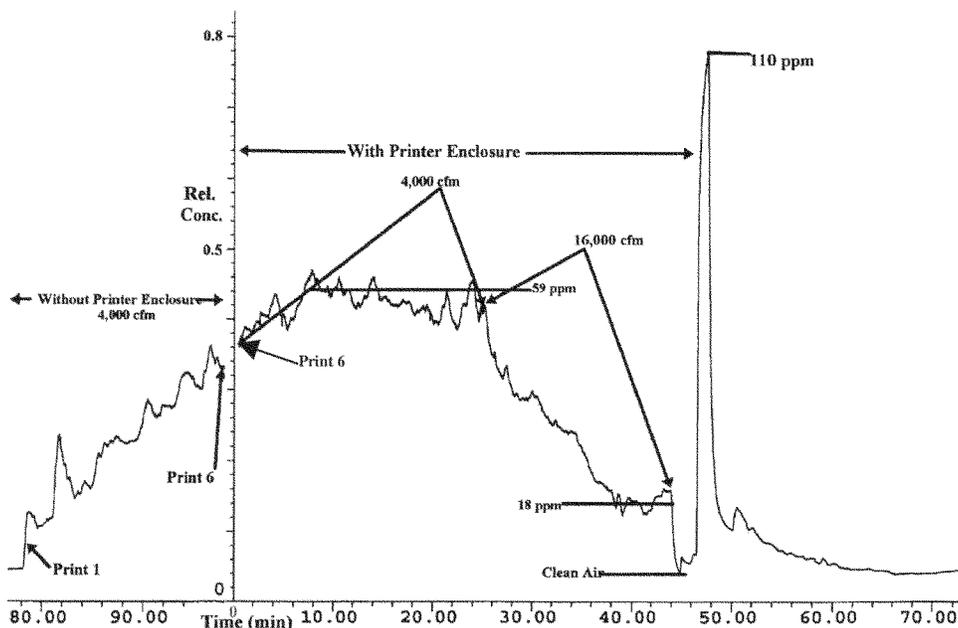


FIGURE 12

Concentration of PGMEA with and without printer enclosure and as a function of ventilation rate.

new 12-table production run without the printer enclosure and with 4000 cfm ventilation rate was started. The data from the second production run without the printer enclosure (time 80–96 min) were moved to the left of the start of the GC/MS run in Figures 12 and 13, so the levels at the point where 6 tables had been printed (96 min and 1 min) can be visually compared. The percent of equilibrium level for the 6-table point in the first run was used to predict the second run equilibrium level.

The second example was a production run of a standard curtain design using the four-color process. Five printer units were in use. In Figure 14 the concentration of PGMEA (72 amu ion) is shown, with clean air at 4 min, 100 ppm PGMEA at 6 min, 100 ppm DMP at 9 min, clean air again at 10–12 min, and room air at 12 min. Production started at 9 min, with a ventilation rate of 4000 cfm. The PGMEA builds up to near-equilibrium at approximately 48 min. At 42 min, air was taken from a clean air source

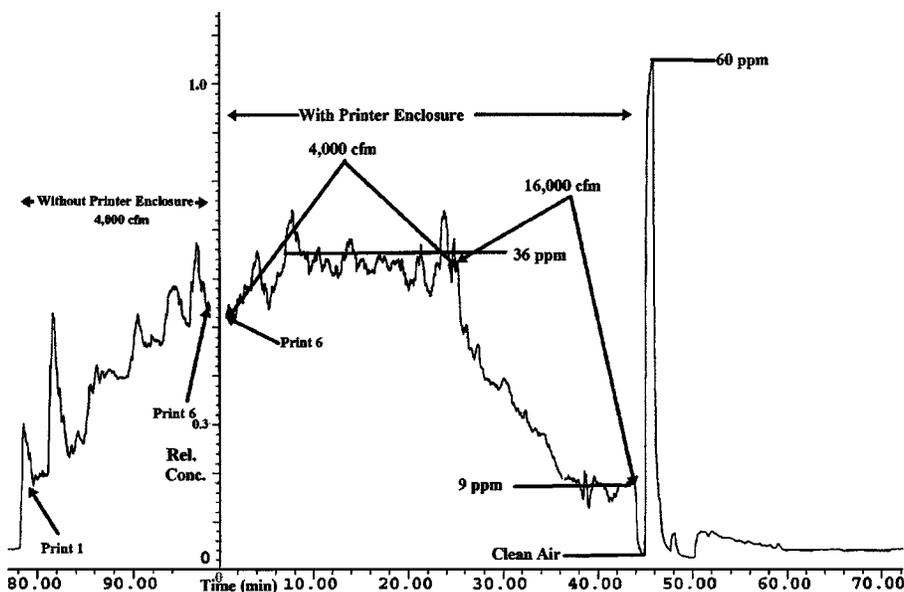


FIGURE 13

Concentration of butyl acetate with and without printer enclosure and as a function of ventilation rate.

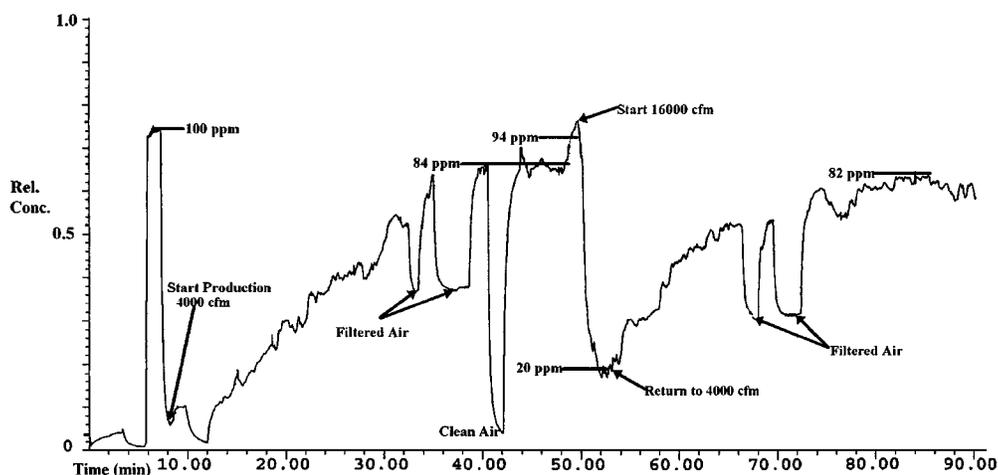


FIGURE 14

Concentrations of PGMEA as a function of ventilation rate.

for approximately 2 min. At 49.5 min, when near-equilibrium concentrations for the 4000 cfm rate had been established, ventilation was increased to approximately 16,000 cfm for 5 min, (appeared to be near equilibrium levels for that flow rate) and then returned to 4000 cfm at 54 min. Concentrations again reached near-equilibrium at approximately 80 min. There were four approximately 2-min time intervals (at approximately 32, 34.5, 66, and 69 min) when air was taken from a partially filtered supply. That data was part of an unrelated experiment and not relevant to this study.

Worker exposures were measured by OBWC using the new ink and with ventilation rates of 4000 cfm (see Figure 15) and 16,000 cfm (see Figure 16). The printer units were not covered.

Cost Estimates of Old and New Inks

Costs were estimated using the new and old ink/solvent systems in a typical production run. The cost of solvent was approximately \$5.50/gal for both systems. The cost of ink base for the old was \$25–\$45 /gal. The cost for time and materials

for making a gallon of new ink in the small-scale in-house process was approximately \$12–\$30/gal, depending on the color (pigment costs can range from \$2–\$20/lb). In a production run of 978 prints using four colors, the old system used 5.4 gal of ink base and 8 gal thinning solvent. The ink cost was \$128 and solvent was \$44, with a total cost of \$172. For the same size run, the new ink use was 6.25 gal (thinned for printing), and 1.75 gal of thinning solvent. The ink cost was \$106 and solvent was \$9.60, with a total cost of \$116.60. Total solvent used with the old system was 10.1 gal (including 75% solvent content in ink base), and the new system used 6.25 gal.

Feasibility of Single-Pass High-Flow HVAC System for Printing Room

With an \$80,000 budget for HVAC equipment, we examined the feasibility of making the necessary HVAC changes for the increased flow ventilation system for the printing room while maintaining desired printing room temperature and humidity control (much better control than the existing system). We also

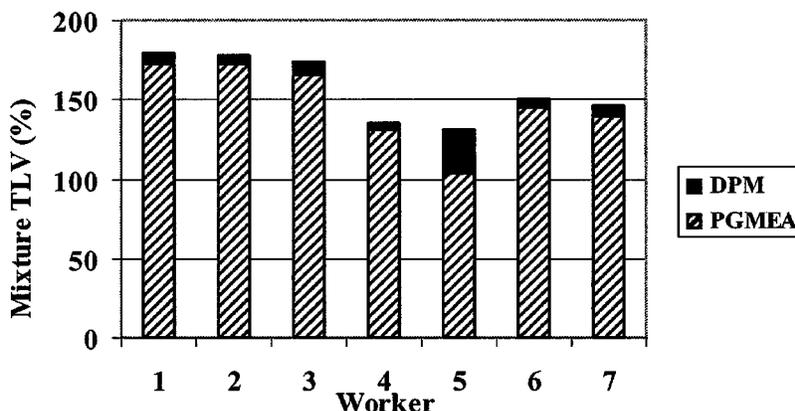


FIGURE 15

Worker exposures using new ink, solvent C, and 4000 cfm ventilation.



FIGURE 16

Worker exposures using new ink, solvent D, and 16,000 cfm ventilation.

estimated the energy costs for the system. The design was based on the need for an adequate flow of clean and conditioned air in order to dilute solvent vapors in the printing room to a level approximately 25–35 percent of mixture TLV levels. Design criteria for the system were based on the following considerations:

- The printing process required that temperature be controlled within a range of approximately 68–75°F and relative humidity (RH) 40–60 percent. The temperature affects drying time and solvent use. The RH affects static electricity problems below approximately 30 percent, and problems with screen deterioration and ink performance from water condensation on the printing screens above 60 percent.
- NOAA records for Cincinnati, Ohio for 1997–1998 showed that the lowest dry bulb temperature was 7°F, and the highest was 98°F (with 77°F average daily wet bulb).⁽¹⁵⁾ Sample outdoor measurements taken at the printing plant on very hot and humid days in June 1998

resulted in a high simultaneous reading of 94°F dry bulb and 80°F wet bulb. Based on the above, we used 10°F as the low temperature, and a maximum wet bulb temperature of 77°F.

- Based on the heat loss measurements for a room adjacent to the printing room having similar insulation to the printing room, the near-zero makeup air heat loss at 10°F outside temperature should be approximately 210,000 Btu/h.
- To control humidity with humid outdoor conditions and outdoor temperatures between 55 and 75°F, operation of the air conditioning (AC) with reheat would be required.
- Heating or cooling of the air would be required under all conditions of operation, except when outside temperatures were between 70 and 75°F, and with RH less than 60 percent.
- For temperatures below approximately 48°F outside dry bulb (saturated conditions yield 44 percent RH at 72°F), added humidity may be needed to raise the RH to at least 40 percent.
- Since the system design has 100 percent makeup air (one pass through building), the thermal mass of recirculated room air existing in typical HVAC systems does not exist. That thermal mass would normally average excursions in duct discharge air temperature resulting from system cycling. Instead, interior temperatures and RH would be a direct result of the heating, AC and humidification/dehumidification provided minute to minute by the HVAC system. Consequently, system cycling would not be permitted.
- Two examples of the printing room, with flow direction and component layout, are shown in Figures 17 and 18. In Figure 17, air enters the room through a large distribution manifold intended to provide low discharge

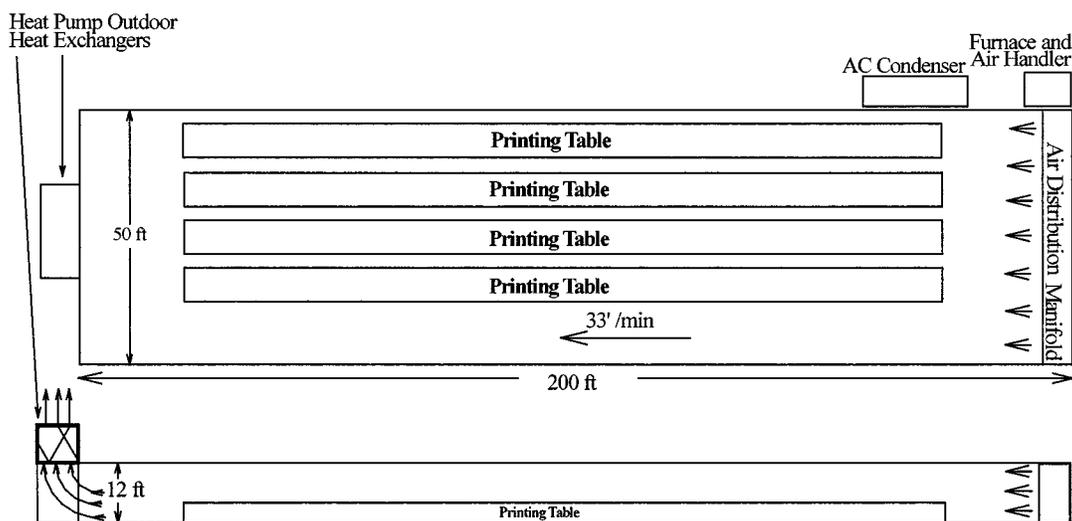


FIGURE 17

Layout of printing room, with HVAC component locations.

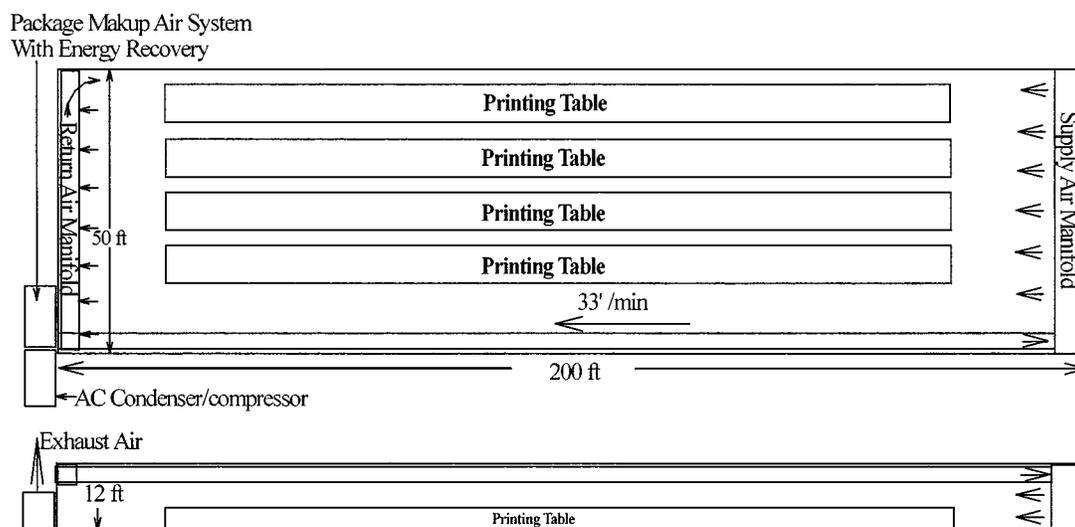


FIGURE 18

Layout of printing room, with HVAC component locations.

velocity air evenly distributed across the cross section of the room. The air enters on one end of the room and flows down the length of the room to an exit (an existing 8×10 ft garage door) and an exterior plenum with an exhaust fan directing the discharged air vertically.

- The system was designed with a flow rate of 20,000 cfm to give a safety margin over the minimum requirement of 16,000 cfm.

System Design Criteria

- Heating should be adequate to maintain a discharge air temperature of 75°F with an outside air temperature of 10°F (approximately $0.12 \text{ lb H}_2\text{O}/1000 \text{ ft}^3$ for 100% RH), and with added humidity to maintain 50 percent RH at 72°F (approximately $0.6 \text{ lb H}_2\text{O}/1000 \text{ ft}^3$). Heating $1,200,000 \text{ ft}^3/\text{h}$ of air to 65°F requires approximately 1,400,000 Btu/h. Evaporating $576 \text{ lb/h H}_2\text{O}$ requires approximately 550,000 Btu/h. Consequently, 1,950,000 Btu/h would be required for maximum heating and humidification.
- AC should be adequate to handle wet bulb temperatures of up to 77°F , and produce a 55 percent RH at 75°F (60°F wet bulb). Resulting enthalpy⁽¹⁶⁾ was approximately 1,270,000 Btu/h. Reheat of air to 70°F would require approximately 320,000 Btu/h (likely to be recovered from refrigeration hot gas circuit). If wet bulb temperatures exceeded 77°F , system flow could be temporarily adjusted downward or production suspended.
- Based on the above, a heating output of 1,950,000 Btu/h and an AC load capacity of 1,270,000 Btu/h should be sufficient.

It was preferred that the air flow through the room with a minimum of turbulence and dead areas. Under those conditions and with the source of vapors distributed along the length of the room in the primary worker-occupied area (along table lengths), the concentrations would build up along the table lengths to a maximum at the end near the air discharge from the building. Worker exposure would then depend on the position history of the worker during the workday, and average exposures would likely be substantially lower than room discharge concentrations. If homogeneous mixing of air in the room was achieved due to turbulence and flow patterns, worker exposures would not depend on work locations in the room and exposure concentrations would be the same as the room discharge concentrations. In either case, the mass-flow of solvent vapors in the discharge of air from the room would be the same. The layout of the room would probably create conditions somewhere between these two models, as there would be some local turbulence created by the workers, the printer units, and other features of the room.

The magnitude of any local turbulence generated is unclear, as are the possibilities of any large-scale recirculation patterns. With minor non-homogeneities, the exposure to a worker would tend to average out since worker locations in the room normally follow a fixed pattern along all tables. The possibility of using fluid dynamics methods to predict concentration profiles in the room was considered; however, it was decided that the complexity of the model would lead to speculative results. As a conservative approach to design, it was decided to assume that dilution ventilation conditions would prevail for the flow design shown in Figure 17. If a significant concentration gradient along the table lengths resulted, worker time-location patterns and certain workstation locations could be adjusted to minimize worker exposures and to possibly allow lower system flow rates.

A single-pass ventilation system with air change rates of those in this study (approximately 10 changes/hr) is unconventional and showed potential for substantial cost savings through energy recovery from the discharge airstream using an air-to-air heat exchanger. Such heat exchangers can have thermal recoveries >85 percent, depending on the cost and complexity of the system. While most of those systems recover only sensible energy, systems able to recover both sensible and latent energy are becoming more popular as they enable substantial reductions in the size of air-conditioning equipment for an equivalent amount of conditioned air. Such systems typically use a rotary media wheel having a hygroscopic media that, in the AC mode, absorb both sensible and latent heat from the incoming outside makeup air stream and discharge the absorbed heat and humidity as the wheel turns into the conditioned air stream exiting the building interior. Figure 18 shows an alternate component layout, with a return air duct leading to an air-to-air heat exchanger for energy recovery. If one assumes a 66 percent recovery of energy during peak air-conditioning loads, the HVAC component capacities could be reduced to 33% of systems not using the technology.

System Components

At least one manufacturer supplied modular makeup air systems meeting the requirements cited above (Thomas & Betts Corp., Memphis, Tennessee). One we examined had a gas-fired heater, blower, filtration, humidification, and refrigeration coil sections in a weatherproof housing that would normally be mounted outside and connected to the building through two air ducts. The refrigeration circuit would normally be connected to a nominal 1,200,000 Btu/h air cooled compressor/condenser unit, pad mounted outside the building. The gas-fired heater portion would have a fully modulating firing rate, allowing for a firing-rate controlled discharge temperature. A modulating hot-gas reheat system was also included for controlling discharge air temperature during air conditioning. The total cost of the major components was approximately \$60,000. The normal practice for the facility was to use a combination of in-house and contracted services for major equipment installation. Based on this, \$20,000 was included for installation parts and labor.

The same system using an energy recovery module (rotating wheel) had similar equipment costs, as the cost of the wheel was nearly offset by the reduced cost of refrigeration components. One example of such a heat recovery system was manufactured by NovelAire Technologies, Baton Rouge, Louisiana. A unit scaled for use with a 20,000 cfm flow rate was estimated to cost \$20,000. An added exhaust blower was required, and additional ducting increased component costs by approximately \$6000. Additional installation costs were estimated as \$7000.

Operating Costs

Calculating the cost of electricity was somewhat complex, with numerous interrelated factors to consider. Under the local utility's demand-sensitive rate, which was typical for industrial users, the peak demand during summer operation was a

basic factor that established the minimum billing and cost/kWh change points for the whole year. A sample calculation using 100 kW peak demand (summer), 40 kW average demand, and 160 h/month operation, yielded an \$8.25/h energy cost for AC. The provisions of the rate structure then allowed energy for all other operations in the facility at \$.054/kWh (existing use approximately 16,000 kWh), as compared to \$.0873/kWh under existing billing. Using gas rates of approximately \$.75/ft³, and an average heating demand of 50 percent of peak heating demand (conservative factor), we estimated an average energy cost for heating of \$7.50/h plus \$.87/h electricity (10 kWh for blowers). Consequently, the costs for heating and air conditioning were similar. Ten percent per year of equipment capital costs (\$6000/year) was used to estimate long-term maintenance expenses. Total operating costs (energy and maintenance) were estimated as approximately \$11/h.

Use of the energy recovery equipment would reduce peak energy demand (lowering energy cost) and average energy use. Manufacturer's data showed an 80 percent recovery of both sensible and latent energy; however, the equipment required approximately 15 kW of additional blower energy requirements. It appeared that 50 percent energy savings would be a conservative estimate, reducing the total operating costs estimate to approximately \$7/h.

The HVAC system described above would be used only during production (typically 35 h/week). Existing ceiling-mounted, gas-fired strip heaters (400,000 Btu/h output) would be used for room heat when the high-flow-rate system was not in use, or as supplemental heat during cold weather to make up for heat loss along length of room while the high-flow-rate system was operating.

Another factor considered was that air discharged to the environment should have as low concentrations of organic solvents as was feasible. This was to minimize the possibility that solvent vapor concentrations would be noticeable to people in surrounding areas. In order to help assure this, reduction of concentrations could be further lowered by the use of entrained outside air in the discharge from the building.

DISCUSSION

Emission Source Measurements

The data in Figure 6 show that, due to their lower vapor pressures and possible solubility differences in vinyl, the decays of MPK and PGMEA concentrations are much slower than for acetone. This is particularly obvious in Figure 7, where the acetone peaks near a fresh print show a rapid evaporation of acetone. One can see the peaks as each color of the print is laid down, with the acetone signal being most time-responsive. While average acetone concentrations in the air were approximately 400 ppm during the run, peak concentrations near the printed ink were up to twice that value and decayed to ambient room air values in about 2 min. MPK and PGMEA concentrations were more constant, due mostly to their lower volatility. Some of the peak

values are also due to vapors released from the passing printer unit, although its residence time over the print is quite brief (10–15 s).

Measurements of the contributions to workroom air solvent vapor concentrations of the printer unit versus the printed vinyl indicated that with ink solvent mixture A, evaporation of solvents from the printer unit contributed approximately 50 percent of the PGMEA vapors and approximately 70 percent of the MPK and acetone vapors (see Table II). A small portion of the solvent vapors indicated as coming from the printed ink were due to evaporation from the ink/solvent mix exposed on the open area of the bottom of the printing screen. It was possible that increased sealing of the bottom of the printing unit could reduce some of that solvent evaporation; however, we saw no practical way to accomplish that. Improvement from such sealing would likely be minimal, as most evaporation from the screen bottom reduced the solvent concentration in the deposited ink.

Printing Screen Changes

Prior to use of the new ink system, increasing the mesh count of the printing screens from 156 to 305 contributed the most to lower solvent use and lower worker exposures. It can be seen that exposures (mixture TLV %) dropped from the approximately 300 percent shown in Figure 3 to approximately 140 percent shown in Figure 9 resulting from the screen changes and changing from solvent mix A to solvent mix B, Table I. Based on the reduced use of ink-thinning solvent, it appeared that the majority of that reduction could be attributed to the change in screen mesh count, as this lowered solvent use by 35–40 percent. Unfortunately, worker exposures were still much too high to eliminate the use of respirators, so the major benefit was a production cost savings.

Solvent Substitution

Attempts to substitute new thinning solvents with the old ink system had limited success. The exposures resulting from a given mixture mixed with ink is a somewhat complex product of the component TLVs and component evaporation rates from the mixture. The evaporation rates depend on temperatures of the room, printing tables and printing screens, air circulation, etc., making the results hard to predict. The revised solvent (mixture B, Table I) did not appear to substantially reduce solvent use or lower worker exposures. Our trial of using MPK as the ink-thinning solvent met technical difficulties that we could not overcome. Even the new NIOSH-developed ink system had similar worker exposures to those shown in Figure 9 when using the same ventilation rates (see Figure 15). The main advantage with the new ink/solvent system was that its “non-photochemically reactive” status allowed a new cost-effective approach to increasing ventilation rates. The principal solvent components of the existing ink were extremely flammable acetone and ethyl acetate. The principal solvents in the new ink were low flammability PGMEA and DPM (NFPA category 2) and butyl acetate,

which was a NFPA category 3 solvent, but with a much lower RER and higher flash point than the existing solvents.

Air Cleaning

A cursory review of air cleaning possibilities showed its major advantage was its likely compatibility with the existing ink/solvent systems. However, it became obvious that incorporating such a system would require a much more complicated HVAC system with a much higher capital investment and operating costs. Larger uncertainties as to worker protection would likely exist, considering the variable removal factors for solvent vapors due to media loading, media aging, media poisoning, possibilities of bed channeling, etc. Constant workplace solvent vapor concentration monitoring would be required, adding to capital investment and operating expenses. The overall complexity of the air cleaning and monitoring equipment would require highly trained operators. These problems made the technology appear impractical for the application, and the approach was not explored further.

Printer Enclosures

The data in Table II imply that, when using thinning solvent mixture A, 50–60 percent of solvent vapors could be eliminated by perfectly enclosing the top of the printer unit. Since mixture B also contained the high-volatility solvents acetone and ethyl acetate, similar results would be expected. Reductions in solvent use using the prototype printer enclosure with ink-thinning solvent mixture B appeared to be significant (35%). The difference between the performance of the printer enclosure and the measurements of the sources of solvent vapors from the top of the printer unit (see Table II) was likely due to leaks in the enclosure and the need to have the tops of the enclosures off for thinning and adding ink. Reducing emissions from the process through the use of controls, including printing screen changes and the enclosure of the printer units, as well as ink-thinning solvent changes, still did not reduce airborne concentrations to a level that would allow discontinued use of a respirator. However, the printer enclosures did satisfy a best available technology (BAT) requirement, which was important to securing new OEPA permits.⁽⁹⁾ When used with the NIOSH-developed ink/solvent system, the results of the printer enclosure were less dramatic, as the emission rates from the printer unit were much less using the lower volatility solvents.

The data in Figures 5 (PGMEA) and 6 (butyl acetate), show the effect of using the printer enclosure and two ventilation rates, 4000 and 16,000 cfm, with the new ink formulation. One ink color and one printer unit were used. During the same data collection run, the printer enclosures were removed. Data gathering was cut short after six tables of printing. Comparing concentrations at equal amounts of prints in the runs, with and without the enclosure, the PGMEA levels were nearly equal and the butyl acetate was approximately 20 percent higher without the enclosure. This indicated an overall reduction in solvent

usage of less than 10 percent for mixture D with the printer enclosure.

The difference for the emissions of PGMEA in this instance as compared to PGMEA in the solvent mixture B is probably attributable to a change in the effective RER for PGMEA in mixture B as a result of combining very volatile solvents with low volatility solvents.⁽¹⁴⁾ The data show air concentrations were approximately inversely proportional to the ventilation rate. The data also indicate that the combination of solvent substitutions and the printer enclosure did not reduce solvent vapor concentrations enough to discontinue respirator usage.

Substitute Inks

The substitute solvent/ink system from a European vendor did not result in any improvement, as some of its component vapors were eye irritants and the ink had adhesion problems. Other substitute inks tried also were not workable. The ink/solvent system developed in this study performed as well or better in the production process than the original ink and used ink solvents not considered to be photochemically reactive. The lower evaporation from the printing unit meant a reduced need for solvent replenishing during the printing process. This resulted in the benefit of a more consistent ink viscosity and pigment density throughout printing runs. It also appeared to reduce water condensation on the printing screen, which was normally a problem in the summer. In many printing runs, drying time was slightly greater than for the commercial ink system; however, with the proposed improved environmental controls it was likely that such minor differences could be minimized or eliminated by controlling printing room temperatures and air flow rates over the printing tables.

The existing ink used extremely flammable solvents as principal components (acetone and ethyl acetate). The new ink used much lower flammability solvents. The existing commercial inks resulted in a significant odor being emitted from the newly opened shower curtain, which remained for a few days after first hanging it. The new ink produced less odor and may result in reduced solvent exposure in the home. The cost of ink base in the old ink/solvent system was \$25–\$45/gal. The cost of the new ink, produced in a small scale on site, was from \$15 (white)–\$30/gal (red). The new ink also reduced total solvent use (including solvent in the base ink) by approximately 40 percent compared to the existing ink with solvent mixture B.

Exposure Reduction Achievements

Improvements in the process with solvent, printing screen, and ink changes all contributed to a decrease in workplace solvent vapor concentrations from over 300 percent mixture TLVs (see Figure 3) to approximately 140 percent mixture TLVs using both solvent mixtures B and C (see Figures 9 and 15). Unfortunately, until exposure levels were reduced to levels substantially under one TLV, it was not possible to discontinue respirator use.

The company asked if perhaps 50, 75, or 90 percent of TLV levels would be acceptable for eliminating respirator usage. We explained that there were many factors to consider, including the range of sensitivities of individuals to a chemical, the fact that their process varied day to day, the possibility of extended shifts, more printer units operating, more solvent use due to higher temperatures, different rates of printing, monitoring errors, and that they did not do routine or continuous monitoring. Consequently, they needed a sizable safety margin. We felt that 10 percent TLV levels would be an excellent goal; however, considering capital investment and operating costs, 25–35 percent would probably be acceptable, as measured on a typical four-color process production day.

Nearly all of the company's comments concerning implementing the new ink system seemed centered on how much money it would save, and hardly ever were the goals of improving worker conditions mentioned. We frequently made the point that we were there to solve a problem of worker exposure, and that cost savings were a secondary goal. One of the reasons we spent so much time on their problem was that they were one of the most extreme cases of worker exposure to solvent vapors that we had encountered. Most improvements in workplace conditions justify expenditures; consequently, the company should not focus completely on the amount of cost savings as the condition for making changes. We saw that worker compliance with their respirator program was problematic, and it was not a workable remedy.

Based on both calculation and GC/MS concentration measurements using the new ink in production, the use of the new ink with its non-photochemically reactive solvents and an associated 400 percent increase in dilution ventilation was anticipated to result in reducing workplace solvent vapor concentrations to approximately 10 percent of those when this study started. That would result in airborne concentrations at about 25–35 percent mixture TLVs, which could be acceptable for working without respirators. Tests of the reduction in exposure with an increased single-pass ventilation flow rate in the printing room can be seen in Figures 12, 13, and 14. In all three cases, when the flow rate was increased by a factor of approximately four the concentrations of the measured solvent vapors dropped by a factor of approximately four. The use of the printer enclosure could reduce solvent evaporation further.

Measurements of personal exposures to workers were made by OBWC using five printer units without printers enclosed, the four-color process with the new ink and solvent mixture D, and with a ventilation flow rate of 16,000 cfm. Those measurements showed an average worker exposure of 38 percent mixture TLVs. Considering the measurement errors and the elevation in worker exposure next to the printing units, the measurements tended to support the feasibility of using the new ink/solvent system and a 400 percent increase in ventilation rate to allow workers to work without respirators. Use of the enclosed printers would likely have further reduced those exposures.

HVAC Feasibility

Our study of an HVAC design for the workspace indicated that both capital investment and operating costs for a 20,000 cfm system appeared affordable. Using off-the-shelf commercial HVAC equipment, operating costs of approximately \$11/h were estimated. Use of energy recovery equipment could reduce this to less than \$7/h. This operating expense could be compared to the expense for respirator cartridges of approximately \$7.50/h and operation of the existing catalytic oxidizer at \$34/h (assuming 2000 h/year operation). A capital investment of approximately \$80,000 was estimated (using some in-house installation labor), and \$93,000 using energy recovery components. The existing HVAC equipment was over 15 years old, inefficient, due for replacement, and often unable to maintain temperature control with the existing ventilation flow rates.

CONCLUSIONS

The new ink/solvent system performed as well or better in the production process than the original ink, used ink solvents not considered to be photochemically reactive, and was likely to cost less than the existing inks. Solvent usage was reduced by over 35 percent. The existing ink used extremely flammable solvents as principal components (acetone and ethyl acetate). The new ink used much lower flammability solvents. The existing commercial inks resulted in a significant odor being emitted from the newly opened shower curtain, which remained for a few days after first hanging it. The new ink produced less odor, and may result in reduced solvent exposure in the home. The use of printer enclosures allowed the company to reduce the evaporation of solvents from their printing machines, contributing to cleaner air in the plant and in the plant exhaust, and a cost savings due to a reduction in solvent usage. When used with the new ink system, the enclosures met BAT requirements. These changes allowed the company to apply for a new permit from the OEPA removing requirements for the catalytic oxidizer, and allowing unrestricted ventilation of the workplace. Consequently, working conditions could improve since it would no longer be necessary for the workers to wear respirators. These changes would also preserve environmental air quality. The proposed new HVAC equipment had estimated capital costs similar to what the company had budgeted and estimated operating costs less than one-fourth those for the existing catalytic oxidizer and respirator program.

The overall results of this study contributed to improvements in:

- Worker health—by changes to the ink/solvent system enabling economically feasible changes to environmental control systems that allowed workplace concentrations of solvent vapors to be greatly reduced. That eliminated the requirement for use of respirators by workers.
- Worker safety—by using lower flammability solvents.
- Company profitability—through lower manufacturing costs resulting from the reduction in solvent use, the likely lower cost of producing the new ink, the elimination of respirator usage, and lower operating costs for the environmental control systems.

While this study was oriented toward solving a problem for a particular type of business, the inks developed for shower curtain printing may be adaptable to other types of printing on plastic substrates. Similarly, the methods explored for economical single-pass ventilation of this facility should have broader applications in industry.

This study also highlights the problems of some environmental quality goals conflicting with worker health and safety goals. It shows that the solutions to such problems may require the industrial hygienist to examine the entire process and the regulations the company is operating with to find a workable solution to a worker health problem. The cooperative efforts of the company and local, state, and federal government agencies may be required.

POSTSCRIPT

Working with the company during the research and design phases of this project was a cooperative effort. The company displayed an enthusiastic commitment to making process and HVAC changes necessary to complete the project. However, there then occurred a period of restricted communication and substantial delays in proceeding with the complete changeover. Finally, the company chose to discontinue operation of the facility and selected overseas vendors for the product.

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