

THE DEVELOPMENT OF A VOC-FREE LITHOGRAPHIC PRINTING SYSTEM

Thomas J. Pennaz*

Keywords: Emission, Environmental, Inks, Lithographic, Printing.

Abstract: A pressing problem facing lithographic printing is the development of alternative cleaning methods that minimize emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). The printing industry has focused on developing wash-up chemistries that work with traditional ink chemistry. This paper presents an alternative strategy: the selective solubility of oil-based lithographic inks, which remain water insoluble during printing but convert to water soluble during cleanup. The result is a system that performs lithographically during printing, but uses a zero-VOC, water-based solution during cleanup. This paper discusses ink properties, press performance, and print quality results of the new system.

Introduction

As environmental stewardship becomes a global issue, industry continues to strive for ways to minimize its environmental impact. The printing industry is no exception and has recently factored environmental issues into its decision making. Witness the use of alcohol substitutes, recycled paper and soy inks as changes that were primarily motivated by environmental pressures.

One of the industry's most relevant issues, VOC and HAP emissions related to press and blanket cleanup, continues to pose significant problems. The need exists to replace these conventional cleaning solvents with environmentally friendly products that perform at levels acceptable to the printing industry.

The United States Environmental Protection Agency (EPA) has recognized blanket and roller wash as a significant source of VOC emissions for lithographic printing. The proposed Control Technique Guidelines¹ call for blanket and roller wash with VOC levels below 30% by weight. Although research strives to develop effective cleaners to satisfy this requirement, significant challenges remain to meet the needs of today's lithographic industries.

This paper presents a new approach to this problem and provides characteristics of a new system that eliminates the use of solvents in lithographic press cleaning. The new system consists of a water-washable

*Corporate Scientist, Deluxe Corporation

lithographic ink and a single-phase, water-based cleaner that contains no VOCs.

The Cleaning Requirements of Lithography

Modern press technology and production requirements place heavy demands on cleaners. Blanket cleaning accounts for the majority of solvent consumed. Blankets are washed between plate changes and periodically to remove paper dust, offset powder, excess ink or other contaminants that affect print quality. Blankets are cleaned manually by applying solvent to a shop towel or other wipe that is then applied to the blanket surface to remove ink and other contaminants. Automatic or mechanized blanket washers are available to pump or apply solvent to the blanket. The solvent is then removed by a cloth web, brush, roller or other means.

Press rollers are cleaned when ink needs changing because of color, ink contamination or end of production. During cleanup, the rollers contain a mixture of ink, fountain solution and other contaminants such as paper dust or offset powders.

Other miscellaneous cleaning needs include ink fountains, plates, press side frames, impression cylinders, grater rolls, ink knives and the general press area.

The Solvent Standard

Conventional petroleum-based press cleaning solvents are the standard in the industry. These are effective because they dissolve ink and evaporate quickly. Solvency is an important consideration in cleaning, while evaporation enables a quick restart of presses with no residue left on blankets or rollers.

Petroleum-based cleaners have recently changed in response to safety, health and environmental concerns facing the industry. Whereas methylene chloride, toluene, acetone, perchloroethylene, 1,1,1 trichloroethane and VM+P Naphtha were once common in cleaners, the printing industry has gone to higher boiling aliphatic or low aromatic distillates.

Because they are low-cost, single-phase and evaporative, petroleum-based solvents are the standard by which new cleaners are judged. However, the safety, health and environmental impact of conventional solvents has forced the industry to consider alternatives, including low-VOC cleaners.

Current Low-VOC Technology

Current approaches to reducing VOC content in blanket and roller washes have met with limited success. Three approaches have emerged.

The first involves reducing vapor pressure, which has resulted in terpene, vegetable oil, ester and other organic-based systems. Reduced VOC emissions result from reduced evaporation during the clean-up process. The second approach involves emulsion or water-miscible technology in which VOC content reduction results from diluting the solvent with water. The third approach evolves from conventional detergent technology relying on emulsification and detergency to clean ink from blankets and rollers.

Properties of the Ideal Cleaner

Given the capabilities of current solvents and the safety, health and environmental challenges related to these solvents, the ideal cleaner would have the following properties:

- It would be a single-phase solvent for the ink and other contaminants present during cleanup;
- It would function under ambient conditions;
- It would leave no residue, thus avoiding long makeready, poor transfer, ink contamination and other problems;
- It would be stable, which is necessary for use in automatic equipment;
- It would be available at low cost;
- It would address safety, health and environmental issues.

Water as a Solvent

Although water is not a solvent for conventional lithographic inks, it is effective on paper dust, offset powders and glaze. Paper dust buildup can be significant, especially on uncoated papers, and water has commonly been used in blanket washing to remove the buildup. Water is also used to clean blankets during work-and-turn applications, when powder from the first pass accumulates on the blanket during the second pass. Water is also used to rinse the roller train to remove glaze buildup.

Because most organic solvents leach plasticizers or penetrate rubber compounds, water can extend roller and blanket life if used in place of solvents.

A New Approach

Lithographic inks have evolved from a perspective of print quality and process requirements, such as press speeds, paper quality and dampening system designs. No consideration has been given to cleanup. Similarly, solvent replacement research has accepted lithographic ink as a given and has attempted to develop materials to replace conventional solvent.

Our new approach begins with a fundamental shift, one that no longer views lithography as independent steps but as a process. Press cleanup thus joins optimal press performance and print quality as part of the overall printing process. This shift focuses on all components of the lithographic process, including ink and water balance, print quality, press configuration, plate type, fountain solution and press cleanup.

The lithographic process requires inks that accept water under controlled emulsification but remain separate phases at all times. This requirement is challenged under the severe shear and temperature developed on the press roller train. In addition, fountain solutions usually contain surfactants and cosolvents to reduce surface tension. Moreover, interfacial tensions between the image area/non-image area of the plate and ink/fountain solution must be balanced to achieve good lithographic performance.

When lithography is viewed as a process, it becomes apparent why the industry has struggled to find effective alternatives to solvent-based cleaners. Such is the case with water-based cleaning solutions. Because lithography requires inks with good water stability, inks that are designed to resist water solvency will resist water-based cleaners.

The Concept of Solubility Conversion

Once we focused on the process requirements of lithography, we speculated that a solubility conversion during cleanup would be a viable approach. We then developed a system in which the ink becomes selectively soluble depending on the aqueous liquid with which it interacts. The ink remains water-insoluble when in contact with fountain solution, but converts to a water-soluble state when in contact with a special aqueous wash. As a result, water acts as a solvent for the ink during cleanup and imitates petroleum distillate solvency. This allows single-phase, water-based cleaners that offer the benefits of water described earlier, besides eliminating VOC materials.

As we proceeded with development, we identified four goals. First, to effect the solubility conversion, we desired a chemical key that could be isolated and easily controlled. Second, we wanted to maintain the fundamental lithographic principle of oil and water immiscibility. Third, we wanted to use existing plate, press and fountain solution technology, thus taking advantage of existing technology and minimizing impact on printers. Fourth, to ensure an adequate supply and favorable cost for resulting inks, we wanted to use existing raw materials as much as possible, including oils, resins and pigments.

Solubility Conversion Mechanism

After studying many systems, we concluded that pH was a viable means to effect the solubility conversion of lithographic ink. Our decision was based on solution equilibrium and on our ability to design systems with water solubility as a strong function of pH. In addition, we could design amphoteric systems that allowed us to convert the ink over a wide range of pH. Such a system was unaffected by individual salts, surfactants, cosolvents or other fountain solution additives, and pH was easy to measure and would generally remain constant during the printing run, especially with buffered systems. pH was also the most cost-effective and simple means to accomplish our goal. Figure 1 portrays the ideal behavior of this system.

Figure 1
Ideal behavior using an
acidic fountain solution and alkaline wash.

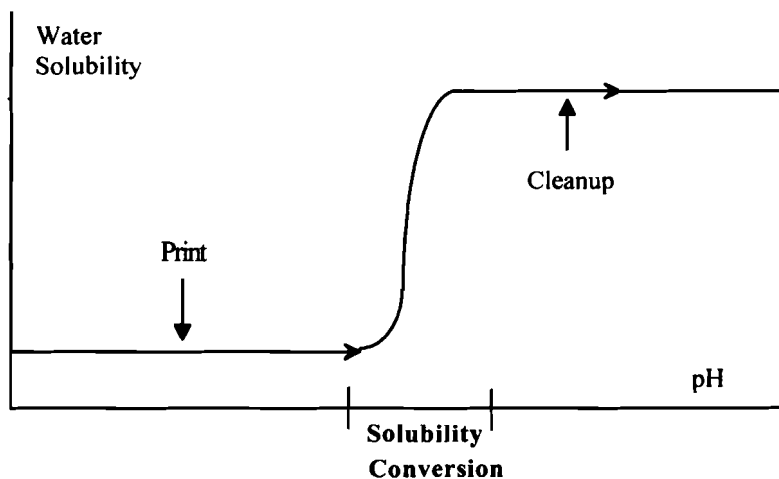


Figure 1 shows the ideal case of water solubility as a step function of pH. It is important to optimize the varnish system to come as close as possible to a step function. In addition, by controlling the functional groups, it is possible to shift the conversion region to any desired pH.

Using functional resins that are inherently hydrophilic required extensive study of varnish chemistry. Even though solution equilibrium

worked in our favor, the shear and need for controlled emulsification in the process offset the effect. Our study resulted in varnish chemistry that is functional yet remains hydrolytically stable on the press when in contact with aqueous solutions at the proper pH. As shown in Figure 1, the print region should be stable over a wide pH range to avoid changes in ink hydrophilicity with minor fluctuations in pH.

The solubility conversion mechanism maintains an oil-based ink system. More importantly, it permits the move to a completely vegetable oil-based ink. Introducing functional resins, coupled with vegetable oils, creates increased varnish stability by overcoming poor compatibility with petroleum solvents. The result is a petroleum distillate-free ink and wash system. We have seen performance improve after removing all petroleum distillates. All common vegetable oils, including soya, linseed, castor and tung, have been used in the ink formulations. Pigmentation, based on dry grind or flush, has remained the same.

Other Benefits

Other benefits include the potential advantage of using conventional shop towels and common laundering techniques. Because they discharge solvents to sewers and vent VOC emissions during washing, many laundering services will no longer take printers' towels. If they do, laundries require centrifuging or other techniques to remove excess solvent. This results in hazardous waste generation for the printer and residual solvent emitted at the laundry. Printers have turned to disposable shop towels, which also raise environmental questions. However, since the new system eliminates petroleum solvents, many, if not all, of these issues have been eliminated.

Furthermore, the selective solubility can be reversed. Because solubility is a strong function of pH, the waste water generated can be treated by moving the pH to the insoluble region for the ink. This results in precipitation of the ink as particles removed by filtration. Laboratory studies indicate more than 99% efficiency in removing ink by pH shift and filtration. This process also removes all ink components, including oils, liquid components and pigments. Figure 1, read right to left, depicts this behavior.

In addition, the new system addresses employee safety and health issues. Although the press cleaning solutions are slightly alkaline or acidic, they are non-corrosive, safe and free of fire hazards and hazardous air pollutants. Moreover, the new system results in pollution prevention, by eliminating emissions and waste from the source. Also, as we develop the water treatment methods, any waste generated can be treated

efficiently, thereby reducing the volume of waste. Transportation is easier due to the nonhazardous nature of the products.

Finally, because solvent storage areas are no longer necessary, the new system may make it possible to store press wash on the press room floor along with fountain solution.

System Approach

The new concept requires viewing the ink/fountain solution/wash as a system. Of the three components, the ink is the most critical, the wash is the second, and the fountain solution the third.

The wash merits special attention because it provides many of the benefits found in the system. For example, it is completely water-based with no cosolvents. The alkaline wash system has a pH of 9.0 to 9.5, which minimizes employee health and safety issues that may result from high pH solutions. While surfactants are important to break the surface tension of the water, it is desirable to identify surfactants that do not leave any residue. The wash uses a surfactant system that improves wetting but does not leave a residue or hinder the waste treatment process.

Moreover, the wash does not harm blankets or rollers and is extremely effective at removing glaze, paper dust and other contaminants. The wash does impact the reversal process used to remove ink from water solutions. Lastly, the wash is low cost.

Fountain solution is the least critical of the components because of the pH mechanism. Printers will have fountain solution preferences, just as they do with conventional inks. For acidic solutions, we have found optimum pH to fall between 4.0 and 5.5 -- well within the normal operating range of most solutions.

We have tested a matrix of solutions with good results. The matrix consisted of metal plates, silver-based plates and electrostatic plates, with associated etches. We tested each of the chemistries with alcohol, alcohol substitutes and alcohol free. We also tested zero-VOC fountain solutions with good results. The system is currently used in production with various plates and fountain solution combinations.

Print Characteristics

We obtained the print characteristics of the inks from a production setting in order to present an accurate picture of performance. Moreover, although we compared commercial products with products based on the new concept, we will not present these comparisons. Our intent is to focus on the new system.

Our primary concern was the emulsification behavior of the inks. Although controversy exists over the value of water pickup and

emulsification tests, these tests do provide a means to discuss such behavior.

Table 1 outlines the water pickup and emulsification behavior of a set of commercial sheetfed inks based on the new technology. Although the water pickups are average, they remain constant over time. In addition, the actual printing of the inks has proven good ink/water balance and stability.

Table 1
Commercial Sheetfed Inks
(Tack sequence 16-12, viscosity 250-350 poise)

Ink	Water Pick (Duke) 400 Strokes - % Water
Process Black	54%
Process Cyan	54%
Process Magenta	48%
Process Yellow	36%

Because printers buy ink for its printing and not its wash-up performance, the industry emphasizes print quality and press performance. We recognized that we could not compromise print quality standards and press performance characteristics in favor of wash-up performance.

We printed samples on a Roland-Mann 600 press and used a GATF test form to measure the reported values. The stock was 80-pound matte, and the fountain solution was Anchor MXRS mixed at 4 ounces per gallon. The print was analyzed using a Greitag D196 densitometer.

Table 2 shows the printing characteristics. The values were obtained from an actual production run, not a laboratory press run. We continue to rely on production results to gauge performance. The results depict an average run; increased and decreased results were obtained on other runs, depending on press condition, plates and other variables. Performance continues to improve as we develop the concept.

Table 2

Color	Density	Hue	Dot Gain 50% (150 Line)	Print Contrast
Black	1.6	---	20%	40
Cyan	1.3	22	18%	35
Magenta	1.4	48	26%	29
Yellow	0.9	7	18%	26

Trapping		Gloss <i>Printed on Champion cast-coat paper Paper Gloss = 61.2</i>	
Cyan-Magenta	73%	Black	87.6
Cyan-Yellow	86%	Cyan	84.2
Magenta-Yellow	72%	Magenta	87.3
		Yellow	88.7
		3-Color	87.4
		4-Color	90.1

We also studied the ink/water balance and latitude by achieving density and then lowering the water speed until scumming first occurred. Density was measured as a function of water speed increases at constant ink setting. The press was brought back to optimum ink/water balance and density fluctuations were not observed through the run. We conducted the test one color at a time and the results appear in Table 3.

Table 3

Press Balance			Water Speed %		
Ink	Density	Water Speed	Scumming Water Speed (%)	Density at Water Speed	Density at Water Speed
Black	1.32	55%	42%	1.22 @ 75%	1.16 @ 85%
Cyan	1.03	47%	35%	0.99 @ 55%	0.92 @ 60%
Magenta	1.06	50%	40%	1.00 @ 60%	0.92 @ 65%
Yellow	0.88	52%	45%	0.88 @ 60%	0.77 @ 70%

Note: The press used was a 40-inch Roland-Mann 600 fitted with a Rolandmatic dampening system.

As Table 3 shows, all inks had a minimum operating window of at least 20% of the dampener speed control. For this press, this was acceptable because we isolated the water feed rate and could adjust both ink and water feed rates during normal operation. Density was run at the printer's prescribed density; similar results were obtained at higher densities.

We studied ink set characteristics using Akira R1-2 proof press. The test was conducted by producing a test proof 1 1/2 by 8 inches long on King James 80-pound cast-coat stock. We then cut the strip into eight pieces. Each test piece was then placed between two sheets of stock and passed through the roller nip of the proof press at timed intervals. The ink is set when little or no ink is transferred to the sheet facing the wet ink film. Table 4 shows the set times of process color sheetfed inks when using the stock. The inks tested were 100% vegetable oil with no petroleum distillates present.

We considered this an aggressive ink set test. Subsequent "live" production runs using various stocks have also been favorable and have allowed printers to work and turn and process the printed goods under normal work routines.

Table 4

Ink	Set Time on Stock
Process Black	4 minutes
Process Cyan	5 minutes
Process Magenta	7 minutes
Process Yellow	4 minutes

Wash Performance

We used a standard test to measure wash-up performance. We used a standard volume of ink and measured the time and the quantity of wash required to clean a press roller train. We have seen good correlation between the standard test and our experience in production on a variety of presses and roller train configurations. Table 5 gives the results of roller wash comparisons.

Table 5

Wash	Ink	Wash VOC Content %	Time Required Min. - Sec.	Volume Required
Aliphatic Solvent	Conventional Soy	100%	2:45	25 ml
Water Miscible	Conventional Soy	75%	2:53	35 ml
Vegetable Oil	Conventional Soy	30%	7:46	45 ml
Emulsion	Conventional Soy	25%	6:00	45 ml
Deluxe	Deluxe	0%	3:16	25 ml

Note: Test is based on removing 9 grams of ink from a Riobi 500K offset press.

As Table 5 shows, the times for the new system were slightly higher than 100% VOC products, but the new system required considerably less time than low-VOC products.

Additional tests for blanket cleaning and general press cleanup have been more subjective than quantitative. However, experience in production, on manual and automatic blanket washers, has been favorable. The

aqueous wash has been used on Heidelberg, Baldwin, Oxy-dry and Deluxe automatic systems. The Oxy-dry system created some problems because the web carried away the wash. It was necessary to adjust the volume of applied wash to minimize curl of the web when using uncoated bond papers.

Development Status

We have tested the new system in various lithographic applications, including business forms, coldset web, commercial sheetfed, folding carton, news, commercial heatset and publication heatset. Table 6 shows the applications for which we have proven the feasibility of the concept, conducted production trials, or used in actual commercial production.

Table 6

	Proven Feasibility	Trials	Commercial Production
Business Forms	X	X	X
Coldset Web	X	X	X
Commercial Sheetfed	X	X	X
Folding Carton	X	X	X
News	X	X	
Commercial Heatset	X	X	
Publication Heatset	X		

In addition, the inks have been coated with aqueous overprint varnishes. We have developed spot varnishes for use with the inks. Also, ultraviolet overprints and foils have been used successfully. The inks are safe to use with laser printers.

Production Results

The system has been extensively tested in Deluxe facilities. Deluxe's business is short-run forms and checks, using highly automated equipment in standard run lengths of 284 impressions. Deluxe requires first-sheet quality with no makeready. Standard production cycle includes

printing, cleaning the blanket, removing the old plate, inserting the new plate and restarting. This cycle occurs every 2 minutes 50 seconds on more than 500 presses in more than 50 facilities. Deluxe cleans blankets more than 20 million times per year. The new system works in this environment without compromising efficiency or quality. It is also performing well in Deluxe web houses and sheetfed applications.

Environmental Implications

The new system has extensive environmental implications. Data from Deluxe and EPA-conducted case studies reveal a significant reduction in VOC emissions resulting from both the press wash and ink solvents. Tables 7 and 8 show EPA test data that appear in the proposed CTG².

Table 7

Conventional VOC Emissions (Lbs/year)				
Model Plant (Medium size)	Ink		Cleaning Solution	
	Use	Emissions	Use	Emissions
Coldset Web	80,000	12,000	22,000	22,000
Commercial Sheetfed	12,000	220	16,000	16,000
Business Forms	12,000	220	16,000	16,000
Folding Carton	12,000	1,400	16,000	16,000
Newspaper	276,000	1,400	16,000	16,000

Table 8

Deluxe VOC Emissions (Lbs/year)				
Model Plant (Medium)	Ink		Cleaning Solution	
	Use	Emissions	Use	Emissions
Coldset	80,000	Approx. 0	22,000	0
Commercial Sheetfed	12,000	Approx. 0	16,000	0
Business Forms	12,000	Approx. 0	16,000	0
Folding Carton	12,000	Approx. 0	16,000	0
Newspaper	276,000	Approx. 0	16,000	0

Table 9

Total Reduction Using New System	
Model Plant (Medium size)	Lbs/year
Coldset Web	34,000
Commercial Sheetfed	16,220
Business Forms	16,200
Folding Carton	16,200
Newspaper	17,400

As the EPA data suggests, even medium-sized plants generate significant emissions related to ink and cleaning solution use.

Deluxe's experience indicates the environmental impact of the new technology. As a short-run printer, Deluxe's blanket wash emissions are significant. Since implementing the new system, Deluxe has eliminated more than 125 tons of VOC emissions resulting from ink and press wash. Many Deluxe facilities no longer require air permits, and the company's overall regulatory burden has fallen significantly.

Conclusion

This paper has presented an alternate approach to the problem of VOC and HAP emissions stemming from the lithographic printing process. The alternate approach is based on viewing lithography as a system of interdependent components. The system incorporates a solubility conversion mechanism in oil-based lithographic ink, by which the ink remains water insoluble during printing but converts to a water-soluble state during cleanup. The result is a system that performs lithographically during printing, but requires a zero-VOC, water-based solution during cleanup. This paper has presented the ink properties, press performance, print quality results, and environmental impact of the new system.

Acknowledgments

The author acknowledges the efforts of a dedicated team of researchers, who continue to assist in developing a concept that was entirely new to everyone two years ago. The author also thanks Dr. Frank Civardi for his complete unwillingness to accept anything without proof and for his continued help and support.

References

- 1) Control of Volatile Organic Components from Offset Lithography (Draft), September 1993, United States Environmental Protection Agency, Page 2-14
- 2) Control of Volatile Organic Compounds from Offset Lithography (Draft), September 1993, United States Environmental Protection Agency, Page 5-3