

Direct Computer To Plate Printing

*Daniel F. Gloster and Michael A. Andreottola
American Ink Jet Corporation
Billerica, Massachusetts*

Abstract

American Ink Jet has developed inks for two completely different printing methods that could make computer-to-plate printing an inexpensive reality. One ink is designed to print onto a diazo resin coated lithographic printing plate while the other is designed to print directly onto the aluminum surface of a lithographic printing plate. Both inks can be printed through a piezoelectric ink jet printer and are capable of producing robust images on lithographic aluminum plates. The lithographic plates produced have been projected to generate tens of thousands of offset impressions. Additionally, high resolution is ensured because the dot size for both inks is approximately 55 μm to 60 μm . The first method, in which the ink is printed onto a coated lithographic plate, is a four-step process. Step one: the desired image is printed onto the photosensitive diazo layer of an aluminum lithographic plate. As the image is printed, the ink undergoes a chemical reaction with the diazo resin coated surface. Step two: the image, now hydrophobic after the reaction, is fixed to the lithographic plate by a heat treatment. Step three: the plate is washed with an aqueous developer so that only the hydrophobic image remains on the lithographic plate. Step four: the image is rendered permanent by a post-development bake. In the second printing method, ink is printed directly onto the aluminum surface of a lithographic printing plate. In this process, the ink reacts with the aluminum surface to form a robust hydrophobic polymeric image.

Introduction

To obtain a print from a subtractive lithographic plate a hard copy of the intended final product must be printed, proofed, and then photographed. In many cases the photographs are developed offsite. The negative images of the photographs are then placed onto the surface of an aluminum lithographic plate coated with a photosensitive emulsion. The plates, protected by photographic negatives, are then exposed to ultraviolet irradiation. The high energy light reaches only the surface of the photosensitive emulsion

that corresponds to dark portions of the original photograph (i.e., text and graphics).

Light striking the surface of a photosensitive emulsion initiates a polymerization reaction. Polymerization causes a high degree of cross-linking that produces a hard and durable polymer image that is capable of transferring thousands of impressions. Post exposure, the entire plate is washed with developing fluid. The regions of the photosensitive emulsion protected by blackened portions of the negative wash away leaving a hydrophilic aluminum surface. The portion exposed to ultraviolet irradiation has become a hardened polymerized oleophilic image that can transfer ink to a receiving medium.

While the process of producing an image on lithographic plates is dominated by photolithography, there is great demand for improvement of this technology. Many have recognized the inability to transfer directly and efficiently from a computer screen to a lithographic printing plate. If, for example, errors are missed in proofing or are introduced during photographic development, then at least a portion of, and possibly the entire process; printing, proofing, photographing, film development, plate exposure, and plate development, must be repeated.

Direct computer-to-plate systems, described here, are based upon a jetted ink that either effects a chemical change in a coating of a lithographic plate that is differentiated upon development or solidifies upon contact with a lithographic plate. Some benefits of direct computer-to-plate printing include reduced cost in producing an image, reduction of time necessary to bring an image to market, much greater flexibility in editing an original image, and elimination of the need to use and dispose of photographic chemicals.

McCue¹ et al. and Gerber² et al. describe a photomask system. In their system, the ink jetted onto the surface of a photosensitive emulsion protects the underlying resin against polymerization by absorbing the high energy ultraviolet energy. Upon development the ink and the emulsion it covers is washed away leaving hardened polymer in the non-imaged regions of the lithographic plate. Furukawa³ describes a polymer coating of a lithographic plate that is rendered insoluble by jetting an aqueous ink comprising metal ions. Using a similar technique, Ma⁴ et al. describes jetting an esterification agent that reacts with

carboxylic acid groups on the polymer to form a water insoluble polymer. The opposite approach was reported by Walker⁵ et al., in which jetting an ink onto the polymer coating of a lithographic plate forms a salt that is washed away upon development. Miyabe⁶ et al. describes a hot-melt system in which the plate is etched after being imaged with hot melt ink.

Systems that do not require developing have also been described. Zerillo⁷ reports a hot melt system designed specifically to eliminate plate development. Hallman⁸ et al. Arimatsu⁹ et al., and Adler¹⁰ et al. have described inks that harden upon exposure to ultra violet irradiation. Additionally, Hallman⁸ also reports that chemical catalysis can initiate polymerization of the ink. In separate patents Blake¹¹, Garbarini¹², Cords¹³, and Kellett¹⁴ all describe the use of Werner complexes in generating lithographic printing plates without the need for development.

Results and Discussion

Herein we describe the development of two methods of direct computer-to-plate printing; one that requires plate development and one that does not. Described in Part 1 is an ink that can be printed directly onto the surface of a commercially available lithographic plate. The coating on these plates consists of a photosensitive diazo resin and a latex carrier resin, 20% and 80 % by weight, respectively. Described in Part 2 is an ink capable of printing onto the bare aluminum surface of a lithographic plate.

Part 1

Exploiting the chemistry of the diazonium group was our strategy in developing an ink that would substitute for ultraviolet irradiation used in classic lithographic plate making. Aryl diazonium salts, prepared by treating

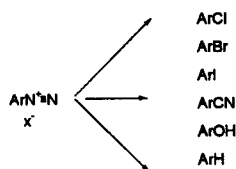


Figure 1. Substitution reactions of diazonium salts.

aromatic amines with nitrous acid, are known to undergo a variety of reactions (Figure 1). Most important for the lithographic industry is the photo-decomposition of the aromatic diazonium (Figure 2).

In addition to substitution reactions, diazonium salts can couple with carbon nucleophiles to give azo

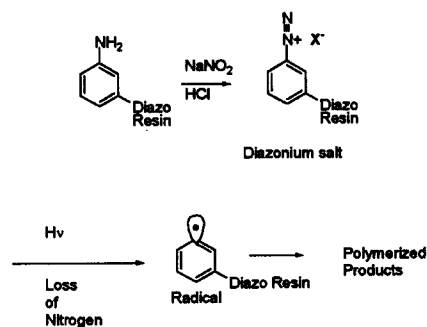


Figure 2. Diazotization of polymeric aromatic amines to give diazonium salts that can decompose to radicals.

compounds. Azo coupling, a reaction famous for producing many beautiful dyes, is the reaction manipulated to produce an ink capable of substituting for ultraviolet irradiation in classic lithographic plate production (Figure 3). A carbon nucleophile and a diazonium salt must be in proximity in order for coupling to occur. Phenolate anion and anilines are typical carbon nucleophiles in azo coupling (Figure 3). To use ink jet in this instance, the ink

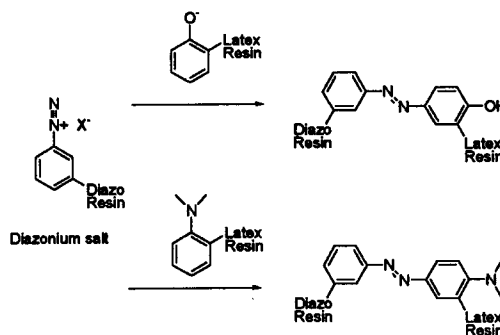


Figure 3. Azo coupling between a polymeric diazonium resin and a polymeric latex resin

must generate a nucleophile attached to the latex carrier resin that cross-links, by azo coupling, with a diazonium salt that is part of the photosensitive portion of the emulsion. Since diazonium salts are stable at low pH, nucleophiles were masked as either phenols, aromatic amine salts, or a combination of both species. Raising the pH of this photosensitive emulsion by jetting a basic fluid onto its surface generates both phenolate anion and free aromatic amines. The latex polymer is hardened by the cross-linking achieved by nucleophilic coupling between a latex bound carbon nucleophile with a diazonium salt appended to the photosensitive portion of the emulsion.

In addition to standard ink jet ink variables, printer/ink compatibility, pH vs. reaction speed and %

coupling (% coupling was inferred by examining the durability of the developed image) were also investigated. To determine if a printer and its parts could withstand a highly basic ink, four inks of different pH ranging from 9.0 to 11.0 were loaded into a Epson Stylus 3000 printer and printed every three hours for 4 weeks. Visible microscopy showed that the printheads were not damaged by inks with high pH (Figure 4).

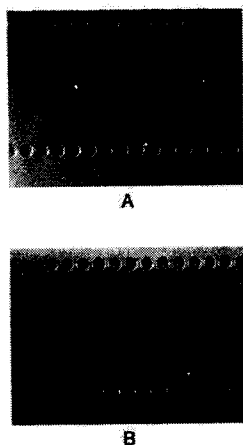


Figure 4. A. Epson Stylus 3000 printhead prior to jetting a pH 11.0 ink. B. One month of jetting a pH 11.0 ink.

To investigate pH vs. reaction speed and % coupling, six aqueous solutions, one each with a pH of 8, 9, 10.2, 10.8, 11.5, or 11.6 were swabbed across the surface of the photosensitive coating of a lithographic plate. After five minutes the swabbed areas were patted dry and then the plate was developed. Each fluid marked the plate but none were capable of producing a rubfast image. Heating the plate after the aqueous base was applied would likely increase the rate of the azo coupling reaction and therefore improve the durability of the developed image by increasing the degree of coupling. A new experiment was conducted in which the plate was heated before being developed. All of the images had improved and similar durability characteristics. For the pH range studied, these experiments made it clear that heat, not pH, was the factor limiting the speed and quantity of the azo coupling reaction. A time vs. temperature study showed that between sixty and ninety seconds at temperatures between 85 °C and 95 °C was the optimum time and temperature to facilitate azo coupling.

Pressruns with plates made by this process were not capable of transferring more than five thousand impressions and in some case transferred as few as fifty impressions. A post bake of the developed image was included into the process to improve the durability of the image. Compared to the initial heating of the plate, which is energetic enough only to facilitate azo coupling, the second heating was designed to decompose the diazonium group.

Approximately one minute at temperatures between 160 °C and 180 °C is the optimum time and temperature range for thermal decomposition of the remaining diazonium salts. This process produces highly reactive species that further harden the image by polymerizing with the latex support. Both mechanisms of polymerization are necessary to produce an image capable, by estimation, of transferring between eighty and one hundred thousand impressions.

A well cured image requires penetration of the emulsion by a basic ink, azo coupling between the photosensitive polymer with the latex support, and finally generation of highly reactive aromatic species by thermal decomposition of the diazonium salts to complete the polymerization process.

To determine which ink components would likely penetrate the emulsion without dissolving either component of the emulsion, a series of compatibility studies were begun. Since the diazo resin is interspersed through the latex support, partitioning of the emulsion is possible but completely unacceptable. Any partitioning of the layers greatly reduces the durability of the image by decreasing the degree of cross-linking between the photosensitive resin and the latex matrix.

Inks were formulated with components that penetrated but did not selectively dissolve the photosensitive emulsion. Dot size and shape were optimized as were ink reliability, resolution, and run length. In order to ensure high quality printing the target size of our dot was 55 µm in diameter.

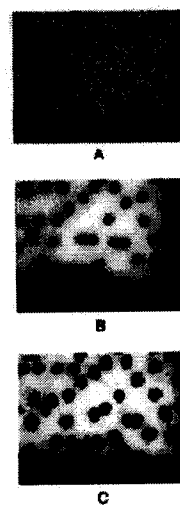


Figure 5. A. Developed dots on a lithographic plate. B. Proof on Mitsubishi Glossy Paper; printed with Epson black ink. C. Press results from plate A.

Figure 5 shows a comparison of dots produced by our final ink on aluminum with both press results and the

proof. The proof was printed with Epson black ink on Mitsubishi glossy paper. The dot size on the aluminum plate (A), 52 μm , is smaller and more round than the dots obtained on the glossy proof (B), 59 μm . The final product from the pressrun gave (C), 64 μm dots. Some of the dot gain is attributed to over inking on press. Reliability was determined both by accelerated aging studies and by print testing. The physical parameters of the ink did not change significantly even after four weeks in the oven at 60 °C and print quality remained good through out testing.

Figure 6 shows the remarkable resolution this ink can attain. Three point font and reverse five point font are easily read on prints made from lithographic plates imaged with AIJ plate imaging fluid. Based upon the

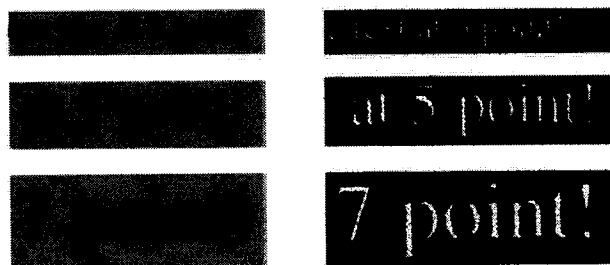


Figure 6. Regular and reverse text.

lack of wear observed on the lithographic plates imaged with AIJ plate imaging fluid, press operators have estimated that our fluid is capable of producing plates that will successfully transfer between eighty thousand and one hundred thousand impressions.

Part 1 Conclusion

Properly formulated, aqueous base, with the addition of heat, can initiate azo coupling that forms an image hard enough to withstand mechanical development. Completion the polymerization process by thermal decomposition of the remaining diazonium salts renders the image permanent. Plates made by this process are capable of producing prints with legible three point text and reverse five point text. Plates made with these inks have shown no wear after transferring over twelve thousand images and have been estimated to be capable of transferring between eighty thousand and one hundred thousand images.

Part 2

Result and Discussion

Printing without the need for development or for working in a light protected environment is the most desirable manifestation of computer-to-plate printing. Part

2 describes our preliminary investigation of an ink to satisfy this criterion.

Werner complexes are acidic chromium metal-carboxylic acid complexes that have been reported to bind with aluminum¹⁴. Inks comprising Werner complexes were formulated and jetted through an Epson Stylus 3000 printer.

Plate A is untreated aluminum and provided the least desirable surface for direct computer-to-plate printing. Although the dots on plate A are round they are unacceptably large, > 200 μm . Plates B, C, D, and E each have proprietary surface treatments and were capable of holding a dot size of 50 μm , 70 μm , 100 μm , and 50 μm , respectively (Figure 7).



Figure 7. Werner-type ink on aluminum surfaces.

Werner-type inks produce high resolution prints that have been used for commercial printing of run lengths greater than fifty thousand impressions. However, the low pH of Werner-type inks has damaged Epson Stylus 3000 printheads and contributed to its poor shelf life.

Part 2 Conclusion

Since Werner complexes are stable in alcohol, an ink comprising a chromium complex would be shelf-stable if, prior to printing, an in-line mixing system combined an alcoholic chromium complex solution with the other ink components. Additionally, the printer and its components must be stable to acidic conditions.

Acknowledgments

We are grateful for the expert assistance provided by Ms. Kerry Fitzpatrick. Her assistance in transporting the images from the microscope to the printed page was invaluable.

References

-
- 1 G. McCue, L. Kans, L. G. Rich, M. E. Guckin, R. F. Croft, J. T. Niland, US Patent 5,156,089 (1992).
 - 2 H. J. Gerber, R. F. Croft, D. J. Sullivan, US Patent 5,495,803 (1996).
 - 3 A. Furukaw, US Patent 5,696,908 (1997).
 - 4 S.-H. Ma, M. W. J. West, US Patent 5,466,653 (1995).
 - 5 P. Walker, S.-H. Ma, A. E. Matthews, US Patent 5,270,078 (1993).
 - 6 M. Miyabe, T. Ohkubo, US Patent 5,852,975 (1998).
 - 7 S. D. Zerillo, US Patent 4,833,486 (1989).
 - 8 R. W. Hallman, K.-I. Shimazu, H. Zhu, US Patent 5,820,932 (1998).
 - 9 S. Arimatsu, T. Hase, K. Kimoto, US Patent 5,312,654 (1994).
 - 10 U. Alder, O. Miller, US Patent 5,511,477 (1996).
 - 11 R. K. Blake, US Patent 3,567,961 (1971).
 - 12 V. C. Garbarini, US Patent 3,716,390 (1973).
 - 13 D. P. Cords, US Patent 3,910,187 (1975).
 - 14 R. M. Kellett, US Patent 5,738,013 (1998).
 - R. M. Kellett, US Patent 5,849,066 (1998).

Biography

Daniel F. Gloster received his B. A. in chemistry and biology from North Adams State College in 1986 and his Ph.D. in chemistry from the University of New Hampshire in 1995 under the direction of Kenneth K. Andersen. Between 1995 and 1999 he conducted research in the area of photodynamic therapy in Dr. James W. Foley's laboratories at The Rowland Institute for Science. In 1999, he joined American Ink Jet Corporation to develop photostable dyes for aqueous ink jet ink.