THERMOPOLYMER LITHOGRAPHIC PLATES FOR IR IMAGING

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Abstract: Digital imaging of lithographic printing plates by near IR exposure (ca 800 - 1200 nm) is attractive from both economic and ecological standpoints, including ambient light stability as well as the prospect for minimal processing requirements. As with other computer-to-plate (CTP) approaches, the utilization of contact masks is also obviated. Exposure with semiconductor diode and YAG lasers has been reported whereby the incident IR photons are absorbed by pigments and/or dyes to produce electronically- and/or vibrationally-excited states, which subsequently cause chemical and/or physical changes in the exposed regions of the coating compositions.

We have developed positive- and negative-working digital plates, which can be utilized for conventional printing with fountain solution, as well as for waterless printing. The imaging processes include (1) ablative in-situ mask generation, thereby converting any analog printing plate into a digital plate, (2) ablation of single-layer coatings and (3) thermal crosslinking. Highlights of our work will be presented with emphasis on high performance compositions. Current studies are directed to minimizing processing requirements.

Introduction

The availability of relatively inexpensive, high power IR lasers, notably diode (830 nm) and YAG (1064 nm) lasers, corresponding plate imagesetters, ambient light stability and the prospect for minimal processing requirements, are attractive aspects of thermal imaging. DeBoer (1995) has pointed out the high quality and reliability of laser thermal printing, including CTP preparation.

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Utilization of IR laser emission for imaging requires the presence of a species which absorbs the IR photons and utilizes the energy to effect a chemical and/or physical change. The energy of photons in the 830 to 1064 nm range corresponds to 145 - 113 kJ/mol (34.5 - 27 kcal/mol), respectively. This energy is likely to be absorbed by population of relatively low-lying excited electronic states which, aside from the possibility of electron transfer (redox) reactions, will be converted into thermal (vibrational) energy by internal conversion processes. Alternatively, the IR photons may be absorbed by direct population of high energy vibrational states. Accordingly, subsequent physical and/or chemical processes will be driven thermally.

Thermally-driven chemical reactions generally occur at all temperatures, albeit faster at higher temperatures. Nevertheless, long times at ambient temperature can result in sufficient conversions to compromise plate performance, notably by reducing processing latitude. In contrast, photochemically-driven reactions can be designed for high thermal stability. Absorption of UV photons of 380 nm, for example, populates electronically-excited states having excess energy of 316 kJ/mol (75 kcal/mol). This level of energy can be utilized to generate reactive species which are essentially inaccessible under ambient conditions or even moderately elevated temperatures.

These considerations have led us to designate reactive polymers for IR imaging "*thermopolymers*" as distinguished from "*photopolymers*," commonly used for UV-visible imaging compositions. We recognize that the long wavelength visible region represents a gray area in this regard.

The potential problem of ambient stability of thermopolymer compositions for IR imaging can be addressed by various strategies. A particularly attractive approach is to utilize processes that require a phase change. Such processes, including boiling (vaporization) and melting, have threshold temperatures, thereby precluding reactivity at lower temperatures.

Secondary phase changes, such as polymer glass transitions, may also occur in relatively narrow temperature ranges. Mixtures of co-reactive polymers can exhibit long-term shelf-life if the Tg of at least one of the polymers is sufficiently above ambient temperatures. Thermal activation above Tg can promote coalescence as well as enhance other processes which require diffusion, such as release of a polymer-encapsulated catalyst. Reactivity can also be controlled by using phase-change catalysts (Pappas, 1991).

Ablative Approaches

Ablative processes are enhanced by the utilization of thermally-unstable and/or self-oxidizing binders, notably nitrocellulose. Carbon black dispersions in such polymeric binders are particularly useful compositions for IR laser ablation. Early disclosures by Scott paper on the use of YAG lasers (1064 nm) to produce lithographic printing plates by ablative techniques utilized such compositions. Methods include:

(1) applying a laser ablatable film on a presensitized plate, followed by imagewise laser ablation to produce an in-situ mask, flood exposure and development of the underlying plate (Peterson, 1979),

(2) laser ablative transfer of an image from an IR transparent donor to a lithographic printing surface, followed by post-bake to cure the image (Peterson, 1976) and

(3) constructing a three-layer coating on an aluminum substrate starting with a crosslinked ink-receptive layer, followed by a laser ablatable layer and overlying silicone rubber ink repelling layer, whereby imagewise laser ablation and removal of the overlying silicone produced plates for waterless printing (Eames, 1977).

Polychrome and others, notably Presstek (e.g., see Lewis, 1994), have advanced these strategies toward the development of commercially-viable digital plate products. Polychrome has developed methods and compositions for converting essentially any analog printing plate into a digital plate, by application of a laser ablative coating which is itself digitally-converted into an in-situ mask (Nguyen, 1997a).

Following flood exposure, the residual mask may be removed during aqueous development of the underlying pre-sensitized (PS) coating. Alternatively, the composite structure may be designed for peel-off removal of the residual mask, which is a useful technique for waterless plates.

The ablatable mask coatings contain IR absorbers, such as Cyasorb IR99 (Glendale) and Epolite IV-62B (Epoline), as well as UV/visible absorbers in order to screen the underlying PS coatings from actinic radiation during subsequent flood exposure. Typical UV/visible absorbers are Savanyl Black (Sandoz) and water-soluble Nigrosine (Spectra Color). Binder resins include cellulosics, acrylics, poly (vinyl alcohol), poly (vinyl pyrrolidones) and various other vinyl copolymers. IR laser doses (830 nm) for in-situ mask generation are in the range of 400-600 mJ/cm^2.

Single-layer ablatable plates have also been developed by novel utilization of polypyrroles, polyanilines and polythiophenes, as well as their derivatives (Nguyen, 1997b). These highly conjugated polymers exhibit strong absorption in the near IR, as well as in the near UV/visible spectral regions, which makes them attractive ablatable materials for both direct and mask plate fabrication. However, the polymers are generally intractable. This problem was addressed by preparing soluble polymer composites and by in-situ polymerization of the corresponding monomer on a lithographic plate precursor.

A pre-formed polymer composite of polyaniline, for example, can be prepared by polymerization of the corresponding monomer (using dodecylbenzene sulfonic acid and benzoyl peroxide), in the presence of a binder polymer, such as poly (methyl methacrylate). Application of the polymer composite to an aluminum substrate provides a single-layer ablatable printing plate precursor.

Alternatively, a binder polymer, such as nitrocellulose, together with a polymerization catalyst, $FeCl_3$, can be applied to an aluminum substrate, followed by vapor deposition of a monomer, such as N-methylpyrrole. The deposited monomer polymerizes on contact with the catalyst. In both cases, IR laser ablation (830 nm, ca. 500 mJ/cm^2), provides positive-working litho plates.

Other direct-to-press approaches include (1) imagewise ablating (CO_2 laser) a hard, hydrophilic coating, notably silicic acid, from an ink-receptive substrate, disclosed by DuPont (Caddell, 1977), and (2) imagewise ablating (diode laser, 830 nm) an ink-receptive polycyanoacrylate ester film (which contains an IR absorbing dye) from a hydrophilic aluminum substrate, disclosed by Eastman Kodak (Burberry, 1997). Both approaches are claimed to provide lithographic plates without the need for further processing.

Thermal Crosslink Approaches

As with ablative approaches, early disclosures were also made on thermal approaches to insolubilize and/or to render imaged areas ink-receptive by IR laser exposure of lithographic plate precursors. Direct production of lithographic plates by thermal cyclization of polyamic acids and related hydrazido compounds to polyimides and derivatives was disclosed by Xerox (Pacansky, 1978). The compositions, with and without added IR absorber (a mixture of IR dye and carbon black), were imaged with a YAG laser, thereby rendering the exposed areas ink-receptive. The imaged plates were directly mounted on a press, without further processing, and were claimed to produce excellent prints with conventional inks and fountain solutions.

Direct to press plates were also disclosed by Hoechst AG (Uhlig, 1977) by imagewise exposure (e.g., utilizing a CO_2 laser) of non-light sensitive hydrophilic films, including poly (acrylic acid) and poly (ethylene glycol), thereby rendering the exposed areas ink-receptive.

Thermal imaging of water-soluble polymer films, including polyamic acids and styrene-vinylpyrrolidone copolymers, which contain IR absorbers, were subsequently disclosed by Lehigh University (Schwartz, 1987). Following mild, aqueous development of the unexposed areas, the litho plates were claimed to provide acceptable prints with good resolution.

In spite of these early results, commercially-viable "no-process" or "on-press-developable" thermal crosslink plates remain as a desirable, but not yet attained goal. Nevertheless, advances have been made. One of the challenges has been to design thermopolymer compositions with adequate ambient stability together with sufficiently rapid reaction rates at the elevated temperatures, but generally short dwell times, of IR laser exposure.

Aside from introducing phase changes, noted above, it is desirable to select reactions for which the Arrhenius kinetic activation parameters, Ea and A, are relatively large. The combination of large Ea and A values is characteristic of reactions having a desirably steep temperature/rate profile (large Ea) and a fast rate at elevated temperatures (large A). These considerations have been applied to the design of thermosetting coatings by Pappas and Hill, 1981.

Reactions in which the rate-limiting step is unimolecular dissociation can have favorably large Ea and A values. Such reactions which produce catalysts, e.g. acid or base, are particularly desirable for imaging since they enhance exposure speed by amplifying the effect of absorbed photons. Chemical amplification in photopolymer imaging systems has been reviewed (e.g., see Monroe, 1994).

Thermal crosslink plates for IR diode laser exposure at 830 nm have been introduced by Eastman Kodak (Walls, 1994) and Polychrome (Quantum 830), which are based on thermal generation of acid catalysts. The acid catalysts are produced from precursors, which are activated by IR absorbing dyes/pigments. The formulations also contain acid-catalyzed co-reactive polymers/crosslinkers, selected to enhance the performance and processing latitude of the plates. Combinations of novolac and resole phenolic resins have been disclosed as co-reactive polymers by Kodak (Haley and Corbiere, 1994). The plates generally require a prebake (between exposure and aqueous alkali development).

We have discovered other classes of co-reactive polymers which are particularly attractive from the standpoints of (1) controlling Tg, (2) introducing functionality for acid-catalyzed crosslinking and (3) introducing groups which promote aqueous development. The resulting plates exhibit wide process latitude and high performance characteristics, notably, high chemical resistance against aggressive UV/EB inks and plate cleaners.

Performance characteristics for preheat plates include (1) good shelf-life, (2) laser dose: 140-160 mJ/cm^2 (Creo Trendsetter, 830 nm), (3) preheat conditions: 120-135°C, 1.5-2.5 ft/min, (4) press performance (including UV/EB inks): ca. 0.4 million impressions (unbaked), 1.5 million copies (baked), (5) fast roll-up and good ink-water balance.

Polychrome is strongly committed to advancing its technology in the thermal imaging arena.

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Literature Cited

Burberry, M. S., DeBoer, C. D. and Weber, S. W.

1997. US Patent 5,605,780 (Feb. 25, 1997)

Caddell, J. R. and Hoehn, H. H.

1997. US Patent 4,054,094 (1977).

DeBoer, C. D.

1995. "Graphic Art Applications of Laser Thermal Printing," TAGA Proceedings, Vol. 1, pp. 29-43.

Eames, A. C.

1977. GB Patent 1,489,308 (Oct. 19, 1977)

Haley, N. F. and Corbiere, S. L.

1994. US Patent 5,340,699 (Aug. 23, 1994).

Lewis, T. E., Nowak, M. T., Robichaud, K. T. and Cassidy, K. R.

1994. US Patent 5,339,737 (Aug. 23, 1994).

Monroe, B. M. and Pappas, S. P.

1994. "Chemical Amplification in Polymer Photoimaging Systems," in Chemistry & Technology of UV & EB Formulation for Coatings, Inks and Paints (SITA Technology, London), Vol. 5, pp. 35-99.

Nguyen, M. T., Zhu, H., Pappas, S. P., Shimazu, K. and Hallman, R. W.

1997a. WO Patent 97/00777 (Jan. 9, 1997).

1997b. WO Patent 97/00735 (Jan. 9, 1997).

Pacansky, T. M.

1978. US Patent 4,081,572 (March 28, 1978).

Pappas, S. P. and Hill, L. W.

1981. "Kinetic Parameter Considerations for Maximizing Stability and Minimizing Cure Temperature of Thermosetting Coatings," J. Coatings Technol., Vol. 53, no. 675, pp. 43-51.

Pappas, S. P., Kuntz, V. D. and Pappas, B. C.

1991. "Latent Amine Catalysts for Epoxy-Carboxy Hybrid Powder Coatings. Investigations on Phase Change Control of Reactivity," J. Coatings Technol., Vol. 63, no. 796, pp. 39-46.

Peterson, J. O. H.

1976. US Patent 3,964,389 (June 22, 1976).

Peterson, J. O. H.

1979. US Patent 4,132,168 (Jan. 2, 1979).

Schwartz, A. M., Kawashima, N. and Zettlemoyer, A. C.

1987. US Patent 4,693,958 (Sept. 15, 1997).

Uhlig, F.

1977. US Patent 4,034,183 (July 5, 1977).

Walls, J. E.

1994. "Unconventional Printing Plate Exposed by IR (830 nm) Laser Diodes," TAGA Proceedings, (TAGA, New York), pp. 259-267.