# **Thermal Imaging: Application in Offset Printing Plate Making**

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### Abstract

This paper reviews various techniques of thermal imaging involving use of infrared lasers. The emphasis is given to various thermal sensitive compositions. The links among these compositions are provided for the purpose of easy digestion for the readers. In some cases, the pros and cons of a particular composition are discussed with regard to commercial applicability.

## Introduction

Most materials undergo certain chemical and physical changes at elevated temperatures. The key to the progress of thermal imaging technology is then two fold. The first is the ability of raising temperature of a medium in a predetermined pattern, and the other is to design chemical and physical changes that are sufficient for a given application, which may require a relief image, or a color image, or an image with different surface properties than the background.

One of the earliest thermal imaging methods is to heat thermal sensitive medium with a black stencil that is irradiated by an IR lamp (1). In this scheme, the stencil functions as a counterpart of photo mask used in photo lithography. Therefore, this method is not amenable to generate digital images in a medium using information directly from computers.

Thermal heads used in thermal printers provide a tool to print digital images by thermal mechanism. A typical thermal head consists of an array of micro resistors that convert electric pulses into heat waves (2). The heat waves from the thermal heads are conducted to thermosensitive medium and trigger designed chemical and/or physical changes in a medium. This mode of selective heating is inexpensive, but has the limitation that a close contact between the thermal head and the medium is required. Reducing friction between thermal heads and medium is one of the concerns in medium design for thermal head image setters (3).

Absorption of a focused radiation, or a collimated radiation beam by an absorbing medium such as infrared lasers as a means for digital thermal imaging was also proposed long time ago (1). Recent developments in solid state lasers have made high power infrared lasers affordable for many applications including lithographic plate making.

For lithographic plate making applications, semiconductor diode lasers emitting in the range from 830 to 870 nm and NdYAG lasers emitting at 1064 nm are two of the most popular radiation sources. For these two radiation sources, numerous thermal compositions have been developed. The majority of these compositions work via thermal mechanisms except for only a few cases such as sensitization of iodonium salt with cyanine dyes (4). Also, the majority of these laser-imaging applications in printing plate are lithographic, with less activities in other printing methods such as flexo (5), gravure (6), and screen printing. This article is intended to put these compositions in perspective.

## **Thermally Sensitive Compositions**

Various compositions for thermal imaging may be classified according to the nature of changes in the medium as a direct result of heating. Useful changes known in the art include the following:

- 1. Ablation etching,
- 2. Ablation transfer,
- 3. Non-ablative chemical conversion, and
- 4. Non-ablative physical conversion.

## Ablation-Etching

Ablation usually refers to a process of disintegrating a medium as a result of thermal decomposition at high temperature and/or as a result of destruction by shock waves during fast perturbation of local temperature. Utilization of the ablation phenomenon to selectively remove inkreceptive coatings on a hydrophilic substrate such as anodized aluminum surface would be the simplest method of laser beam plate making (1). To enhance laser sensitivity, special binder resins such as polycyanoacrylates (7), polyvinylene chloride (8), styrene-maleic anhydride copolymer (9), polyamide and polyvinyl butyral (10) may be used. IR absorbing conducting polymers may be another class of coating materials suitable for single layer ablationtype printing plate (11). After ablation imaging, the leftover image areas can be further cured (12).

Due to relatively high thermal conductivity of aluminum oxide, a small amount of coating residues is often inevitable when using direct ablation techniques. To overcome the heat sink problem, it has been proposed to apply an organic primary layer between the metal substrate and the ablatable layer (13). With this configuration, the primary layer is usually removed by a suitable developer that does not dissolve the ablatable top layer. Similar to this case is the ablation of hydrophobic surface formed on the hydrophobized silver surface, which can be formed through a diffusion-transfer process (14).

An alternative solution to the heat sink problem is to use an ink-repelling non-image surface with heat diffusivity much less than aluminum oxide. This ink-repelling surface could be positioned either below or above the ablative layer. In the event that the ink-repelling layer is placed on the top surface, this surface layer is selectively removed as a result of weakened foundation, which is the ablatable layer and is imagewise ablated by IR laser beam. Silicone elastomer is usually a material of choice for the ink-repelling top surface (15, 16, 17, 18). A lithographic plate with a pattern of silicone coating is used in a so-called driographic or waterless printing where dampening solution on the press was omitted. One of the difficulties involved in this type of printing plates is the removal of loosened silicone coating. Recently, it has been proposed to use an adhesive sheet to facilitate silicone removal from the imaged area (19). Hydrophilic surface coatings in place of silicone have also been proposed (20, 21). The hydrophilic coatings are usually made of organic hydrophilic polymers, or ceramic coatings. Hydrophilic surface of converted diffuse-transfer silver layers has been ablated in this fashion (22). In these cases, the imaged plate can be used on a conventional press with both ink and dampening solutions.

With the medium design that an ink-repelling coating sits on top of an ablatble coating, the imaged plate contains a recessed ink-receptive area. This feature is sometime favorable for reducing dot gain during printing processes. A controlled dot gain is essential for printing high resolution graphics. However, there are applications where appropriate dot gain is helpful for reducing ink consumption while maintaining the color density in half-tone image areas. To increase dot gain, it has been proposed to fill the recessed image areas with a curable composition (23).

One of the major drawbacks of ablation-etching is the requirement for high energy input. To alleviate this problem, light reflecting layer underneath ablatable layers was proposed (24). A more recent advance was made by utilizing interference fringes between two partially reflective layers (025).

In addition to organic coatings, certain IR-absorbing metallic or metallic oxide thin films also undergo ablation when irradiated with high power IR laser (26). These thin films have also been utilized in two-layer printing plates where the topcoat is either a silicone or a hydrophilic coating.

Ablation technology can be also used to generate photomasks, which can be used in imaging conventional printing plates (27). A modification of this technology is to generate a contact mask directly on conventional printing plates (28, 29, 30). This modification has several advantages including saving of film support and direct registration of images on a plate.

#### **Ablation Transfer**

In an ablation transfer process, the ablated materials from an ablatable medium are redeposited into a new coating on a suitable substrate. Because the redeposited coating is usually ink-receptive, hydrophilic substrates are usually used in these applications (31).

The ablation transferred coating usually lacks physical strength. Post-transfer baking may help to alleviate this problem. Alternative way of improving physical durability is to incorporate UV-curing mechanism into the ablatable layer and then irradiate the transferred coating with UV light to effect crosslinking.

It has also been proposed to transfer one reactant on a donor sheet to react with another reactant on an acceptor sheet. An example as such is the pair of silver behenate and a suitable reducing agent (32).

As with ablation-etching, ablation transferred has also be used as a technique for making photomasks. As a matter of fact, both techniques can be utilized in a single imaging step to produce both positive and complimentary negative images. Formation of contact masks on conventional plate is also feasible with ablation transfer (33).

Note that in addition to laser ablation transfer, other heat sources such as thermal heads have also been used to make lithographic printing plate via material transfer (34).

#### Non-Ablative Chemical Conversion

Heat absorbed medium can be used to effect chemical reactions such that the solubility of the reaction product is substantially different from that of the starting material. The solubility can either be enhanced or reduced.

One example of solubility reduction is imidization of polyamic acid in the laser struck areas (35, 36). Other examples in this category include desulfonation of a polymer having sulfo group attached to a conjugated polyene (37), crosslinking between novolac and resoles (38), and deblocking of blocked isocyanate (39). Themal decomposition of some photosensitive compound such as diazonaphthaquinone by laser imaging and subsequent UV flood exposure provide another means of thermal imaging by solubility reduction (40). Negative diazo resins can also be applied in thermal imaging composition provided that a suitable binder resin is present (41). Most of these reactions are irreversible. Zirconia ceramic represent an example of reversible conversion (42). Exposure of zirconia ceramic to Nd:Yag laser (1064 nm) results in hydrophilic-tohydrophobic conversion. The reversal of this conversion is achieved by exposure to CO<sub>2</sub> laser (488 nm).

The direct chemical conversions as mentioned above usually require substantial thermal energy input. Incorporating a thermally more reactive system may help to reduce the energy input, but stability during storage at ambient conditions becomes a concern. This dilemma may be resolved by generating a reaction catalyst such as acid (43), or converting thermally stable groups such as naphthoquinone-diazide into thermally labile groups (44, 45) by other energy sources such UV light right before implementing thermal imaging. This approach has also been applied to waterless plate making, wherein UV-generated acid catalyst is used during subsequent laser imaging to catalyze thermal decomposition of acid labile composition underlying a silicone coating (46).

#### Another solution to the stability-reactivity dilemma is to encapsulate one of the reactants. One example as such is a printing plate having a coating containing a hydrophilic binder and encapsulated reactants. Laser exposure breaks the micro capsules and thereby triggers the reaction of the encapsulated reactants with the hydrophilic binder. The reacted hydrophilic binder becomes ink-receptive and provides the image areas of a lithographic printing plate (47).

A more efficient utilization of thermal energy from a laser beam is to generate catalysts, which then effect more extensive chemical conversion of the medium. For example, onium salts such as sulfonium, iodonium or diazonium compounds can produce strong acid upon heating by an IR laser beam. Strong acid can be thermally generated from sulfo derivatives (48). Some IR dyes can also generate acid upon decomposition during laser exposure (49). An even more efficient way of utilizing laser energy is to design an autocatalytic process where acid generated by laser exposure can catalyze formation of more strong acid. An example of this autocatalytic process is blocked squaric acid (50).

The strong acid during laser exposure can then catalyze crosslinking of phenolic/resole resins (51, 52, 53), or reaction between polyols and crosslinkers with activated ethers (54, 55) and hydroxyimide compound (56). For phenolic systems, added a multifunctional aldehyde may be helpful for acid-catalyzed crosslinking (57). Adding a silicone coating on top of this thermal coating provides a means of preparing digital waterless plates (58).

Thermally generated acids have also been used to catalyze hydrolytic reactions that usually result in solubility enhancement. Examples of materials useful in this application are poly(t-butyl methacrylate), t-butoxycarboxy styrene polymers, polymers with protected COOH groups (59), sulfoimide resins (60), and mixed imide of sulfonic acid and carboxylic acid (61). If an ink repelling silicone layer is placed on top of this type of thermal imaging layer, a waterless plate can be made (62).

Other than thermally generated acid, reactive intermediates such as free radicals, nitrenes (63) and carbenes can also be generated thermally during laser imaging. Photoinitiators have been thermally generated, too. Photoinitiators can initiate free radical polymerization of ethylenically unsaturated compounds such as acrylates and methacrylates during subsequent UV flood exposure. An example as such is the thermal conversion of benzospiran into merocyanin (64).

Lithographic printing plates containing thermal coatings can be modified by applying an ink-repelling topcoat as in ablation-etching methods (65).

Thermochromic materials have been used to generate color images by IR laser beams. If the color images have different UV transmitting characteristics, such thermographic materials can be used as a contact mask on conventional printing plates (66, 67).

#### **Non-Ablative Physical Conversion**

Thermal energy from absorption of infrared laser has also been applied to convert a heterogeneous coating into a more homogeneous coating so that the solubility of the medium is reduced. Usually, the heterogeneous coatings are formed from latex coatings, wherein the latex particles remain dispersed (68, 69, 70). Other heterogeneous systems also exist in patent literature including the case of PMMA dispersed in a phenolic resin (71). Heat generated from IR absorption softens the latex particles and causes formation of a more homogeneous film. The homogeneous film is usually less soluble than the uncoalesced film. Because of this solubility differentiation between exposed and unexposed areas, a negative image can be generated with a suitable developer liquid. To enhance the durability of the developed images, a post-imaging UV or thermal curing may be designed in the system (72, 73, 74). Application of thermal coalesce of dispersed particles has been extended to waterless plate making by adding a silicone topcoat (75).

Another example of non-ablative physical conversion is the change in molecular packing in a rather homogeneous medium. This change may occur when a medium is softened at high temperature and then quenched into a metastable physical state during the cooling process. This metastable physical state features a high free volume content and an internal energy that is higher than the state where intermolecular interactions are maximized. Usually, the metastable state exhibits higher solubility than a true stable state. Although the solubility differentials are not as large as other imaging system, proper selection of developer liquids can make it possible to obtain a good quality relief image. The formation of metastable state may be referred to as a quenching phenomenon, and usually can be reversed by an annaling process. One of the most useful materials for this application is Novolac resin (76, 77, 78).

Thermally induced migration of ingredients between two adjacent layers can be utilized for imaging lithographic printing plates. For example, if the migrating ingredient is a light absorbing compound migrating from top layer to inner layers (79), a contact photo mask is generated and can be further processed as in other contact mask applications. Migration of oleophilic materials from donor sheet to porous hydrophilic aluminum substrate (80, 81) or a substrate coated with sol-gel hydrophilic coating (82) provides a means of making printing plates with little or post-imaging processing.

## Conclusion

In the last couple of years, we have seen an acceleration in patent activities involving thermal imaging. This acceleration is probably associated with the advances made in computers and solid state laser devices. With the current momentum of research and development, we anticipate that before long, thermal imaging will become the main stream for lithographic plate making.

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# **Biography**

Ken-ichi Shimazu received BS from Chiba University, MS from Polytechnic University, and Dr. Eng. from Tokyo Institute of Technology. He joined Polychrome Corporation in 1965 and is the Vice President of Corporate R & D at the newly formed Kodak Polychrome Graphics. His interests include application of digital technology in graphics arts and particularly in the offset plate-making.

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