The Technology Generations of Digital Thermal Printing Plates

R. Goodman*, B. Nüssel*

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Abstract: Digital thermal plate technology developments have been progressing at a rapid rate since the introduction of the first practical thermal plates in 1996. The now fully commercial standard thermal plate requires laser exposure, preheat and chemical processing before a press ready image is obtained. The next generation of thermal plates (no preheat) requires the laser exposure followed by chemical processing (or some sort of combination of chemical and mechanical processing). Further, within the no-preheat concept both waterless and conventionally printing plates are available. The next generation of thermal plates will require only imaging with no external cleaning step (though might incorporate vacuum removal on the imaging device or some "on-press" cleanup). We will discuss the design concepts and issues connected with all three generations of thermal printing plates.

Introduction

Recent publications have highlighted the state of thermal plate technologies based upon the relative commercial viability of the various products. TAGA 98 featured four papers which discussed thermal plates in some detail; some merely highlighted a particular vendor's technology, Herting and Goodman described in detail the plate structural design concept for each major thermal plate product. In TAGA 97 Pappas, et al. gave some detail on the (usually) polymer chemistry design concept behind several different thermal plate technologies.

In this paper we wish to take a different perspective. We will describe the thermal plates from the perspective of the fundamental physiochemical principle, which we believe is utilized in the different thermal plate concepts. Further, we will try to show that these principles all flow from a few basic ideas.

Thermally imageable plates are fundamentally based on a very simple principle: lithographic changes can be made to occur in a chemical medium as a result of significant temperature increases. That is the relative hydrophobicity or hydrophilicity of a coating can be altered by heating, and that such changes can be more or less irreversible within the real time use of the product.

*Kodak Polychrome Graphics

Fundamentally, this is feasible due to two factors. The intense thermal energy that can be created by IR lasers impinging on a narrow area and the typically poor thermal conductivity of most coating materials, ie the inability to dissipate this thermal energy quickly enough to prevent the intense heating of the materials struck directly by the laser. In practice the thermal gradients can be of the order of hundreds of degrees Celsius over tens of microns in lateral distance across a plate coating or ~10°C/micron.

The commercial viability of the thermal plate systems is based on the idea that these systems are not necessarily light sensitive, ie can be handled in normal roomlight, and that many of these thermally alterable coatings are quite robust and give good on-press performance.

There is, however, a fundamental weakness in the thermal plate concepts, IR energies are inherently less than visible or UV light energies. Thus, to achieve the speed of visible light systems developers of thermal plates had to devise clever schemes to provide for amplification of the thermal systems to provide for the full differentiation of hydrophobic from hydrophilic area of a printing plate. It is these amplification system concepts which provide for the definition of the titled reference to "generations" of thermal plates.

First generation thermal plates utilize the fundamental concept of catalytic+thermal reaction amplification. That is, the thermal process merely creates catalytic species, which constitute only a fraction of the sites needed for modifying the hydrophilicity of the coating. A general plate-heating step follows the laser exposure to effect the lithographic change. Somewhat quizzically these plates are called preheat thermal plates. Preheat referring to heating before chemical development; in fact, the heating step postceeds the laser imaging.

Second generation thermal plates are based on the amplification scheme of solubility inhibition. That is, the coating would be soluble but for solubility inhibitors intimately mixed into the coating. The temperature rise causes either chemical change or decomposition of these inhibitors. Thus the coating in the struck areas is now soluble in the developers. There is no need for a "preheat" step because the inhibitor reactions are irreversible in general. However, both the preheat and no-preheat technologies utilize the chemical potential gradient concept to amplify the hydrophilicity differences. That is, the gradient of lithographic change between regions in the coating can be relatively gradual; the chemical interaction with the developer amplifies the difference to give sharp resolution between areas. [Figure 1].

Figure 1a. Laser Energy distribution (Gaussian in time and space)

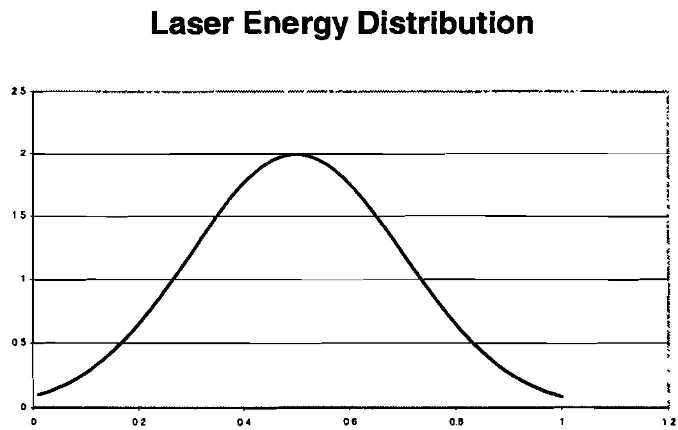
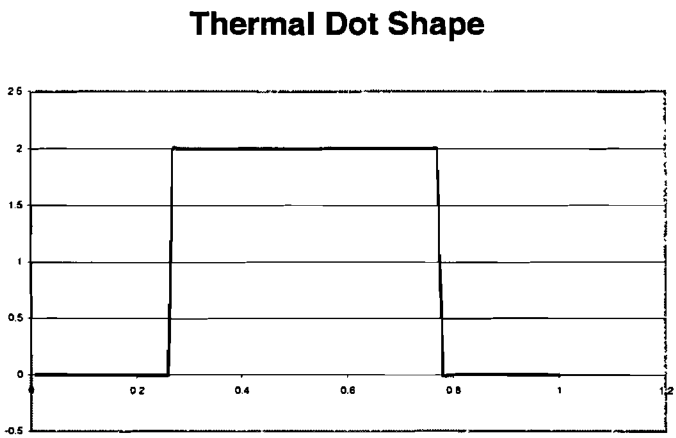


Figure 1b. Dot shape on thermal plate due to threshold characteristic of thermal reactions.



A variant on second generation technology is called ablative thermal technology. Here the amplification step involves either phase change (liquefaction or gasification) or violent discharge of thermally excited materials to effect the lithographic effect. The laser struck areas either liquefy, evaporate or "explosively release" material. A further physical or chemical cleaning is usually necessary to insure the ablated materials don't contaminate the non-struck areas. The decomposition reactions generally require higher thermal inputs than either the catalytic or solution inhibitor decomposing reactions; more of the chemical material in the coating needs to be transformed.

The third generation of thermal plates utilizes various amplification steps. One form of third generation thermal plates is based on ablative thermal technology, but without any further physical or chemical cleaning. Another form of third generation thermal plates utilizes subtle changes in the structure of the coatings to effect the lithographic change. Sometimes called chemical switching technologies these concepts can be variously related to orientational changes, structural changes in functional groups in polymers, etc. The big opportunity provided by these technologies is to allow "Processless" handling before press. That is, these systems could allow putting plates directly on press with no significant chemical or mechanical processing. Further, these concepts would permit direct "on-press" imaging and hence printing without any additional prepress steps. The "no-process" plate has always been perceived as a "Holy Grail" of the printing industry.

The following sections describe in more detail the particular technologies of currently available or proposed plate technologies; conventionally printing (ink/fountain) plates are described first; waterless plate concepts listed second.

Digital Thermal Printing Plate Technologies (for wet offset)

Generation I Thermal Plates

From a printer's perspective first generation thermal plates are described by the necessary process steps to obtain the final image. These steps are IR laser Exposure – Preheat – wet, aqueous alkaline Processing. Each one of these steps provides a part of the necessary total energy to form the final image:

- IR laser exposure	thermal energy (to start the acid-catalyzed crosslinking reaction)
- Preheat	thermal energy (to complete the crosslinking)
- Wet processing	mechanical and chemical energy (to remove unexposed coating)

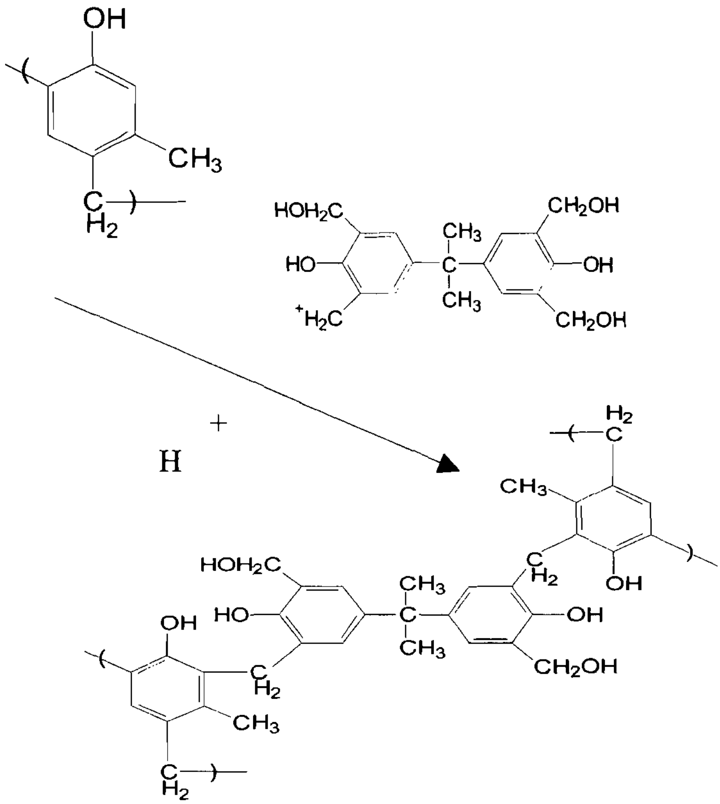
Kodak Polychrome's TP 830 represents the generation I thermal plate in the market, but others like Fuji's Brillia LP-N are following.

A look at the result of a patent search (Table 1) reveals that almost every graphic arts supplier has worked on first generation thermal plates which from a chemical perspective are based on very similar compositions, and function by the same mechanism. The mechanism consists of three major steps: the IR dye sensitized acid generation from the thermal acid generator, the acid catalyzed crosslinking of the phenolic polymers, and the thermal completion of the crosslinking during the preheat step. The essential ingredients in plate formulations of this type are phenolic resins, crosslinker, a thermal acid generator, and IR absorbing dye/pigment. Diazonium salts, diaryliodonium salts, trichloromethyl triazines are examples of such thermal acid generators.

Table 1: Generation I Thermal Plates – Patent Overview

Company	Patent	Composition
Agfa	EP 819,980 EP 819,985	Phenolic – amino crosslinker – latent Brønsted acid – IR pigment (Carbon Black)
Fuji	JP 9197671 EP 795,789	Novolak – resole – acrylic – acid generator – IR dye
Horsell	WO98/31554	Novolak – methylol polyvinylphenol – acid generator - IR dye
Kodak	US 5,491,046 US 5,466,557 US 5,340,699 US 5,663,037	Novolak – resole – latent acid (diazonium salt, triazine)) – Terephthaldehyde – IR dye
Mitsubishi Chemical	US 5,814,431 JP 9244226 JP 9138500	Phenolic – amino crosslinker – acid generator (triazine) – IR dye
Polychrome	WO98/21038	Acrylic – resole – thermal acid precursor – IR dye

Fig.2 Generation I Thermal Plates – Mechanism: Acid-catalyzed crosslinking step



Generation II Thermal Plates

The development of second generation thermal plates was driven by the printer's request to get rid of the preheat oven, and the preheat step. Therefore, describing second generation thermal plates by process steps we find that the total energy necessary to form the final image has to be provided in only two steps:

- IR laser exposure
- Processing

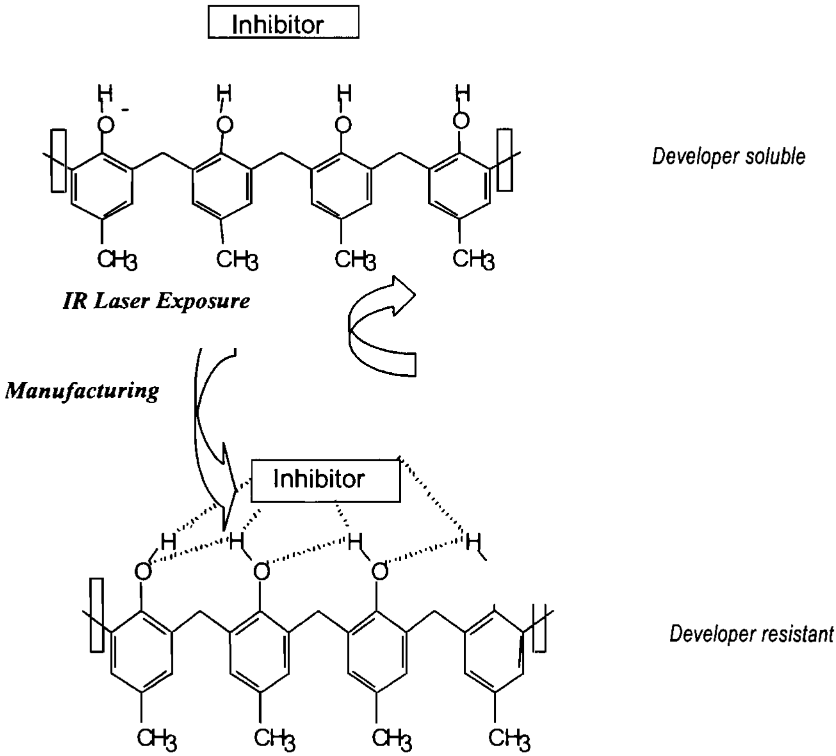
Looking closer at the category of second generation thermal plates we actually find various distinct subgroups, based on either the form of processing (wet or dry), and/or the underlying mechanism.

Sub-group 1: Based on *Physical Insolubilization* (no-preheat, wet processed, positive working)
Various companies independently developed plates based on the working principle of physical insolubilization as the following patent activities reveal (Table 2). The technology utilizes the intrinsic solubilizing properties of conventional positive plate resins (phenolics). The formation of hydrogen bonds between the resin molecules and the insolubilizer/inhibitor during the manufacturing process transforms the coating into the developer resistant form. The rapid heating during the IR laser exposure breaks the hydrogen bonds in the exposed areas, and the solubility mechanism through phenolic hydroxyl groups works again (Fig 2). Kodak Polychrome's Electra or Lastra's Extrema 830 are two commercially available examples of this type of plates.

Tab. 2: Generation II / Sub-group 1 Thermal Plates – Patent Overview

Company	Patent	Composition
Kodak Polychrome Graphics	WO98/54621 WO98/42507 US 5,858,626	Phenolic binder – solubility inhibitor Thermal solubilization
Horsell	EP 825,927	Thermal solubilization of phenolic complex with solubility inhibitor
Mitsubishi	JP 10282643 EP 823,327	Thermal solubilization
Fuji	US 5,631,119	Negative working!
3M	US 4,708,925	Photosolubilization – Phenolic resin – onium salt – IR absorber

Fig. 3: Generation II /Sub-Group 1Thermal Plates – Mechanism



Sub-group 2: Based on "*Thermal Coalescence*"
This technology was originally developed by DuPont, and improved by Agfa, after their acquisition of DuPont's plate business. The not yet commercially available RD9 (N95A) plate from Agfa is an example of this technology. The coating layer contains a dispersion of hydrophobic thermoplastic (heat softenable core / aqueous soluble shell) polymer particles in a hydrophilic binder which coalesce under IR laser exposure to form the insoluble image areas (DuPont - EP 514,145 and EP 599,510; Agfa – WO98/51496, and EP 773,112). A variation on thermal coalescence is described in WO98/53994 by Kodak Polychrome Graphics.

Sub-Group 3: Based on "*thermally induced Developer Action Differentiation*"
Agfa first presented this technology at the 1998 TAGA meeting (Agfa - EP 864,420 and EP 881,094). Based on a two-layer construction on top of a "standard" aluminum substrate, the top layer undergoes a structure deformation

upon IR laser exposure, and then functions as a mask for the alkaline developer. This physical deformation of the top layer not only allows the aqueous alkaline developer to wet the exposed areas of the plate better, but also enables a faster penetration of the developer through this top layer. The underlying polymer layer can be dissolved much faster than in the unexposed areas. This technology demonstrates an interesting aspect of how the total energy to form the final image can be split between laser energy and 'processing energy'. The Thermostar plate can be exposed at rather low laser energies (physical deformations only!); most of the energy necessary to form the final image is provided by the wet processing step.

Sub-Group 4: Based on *Ablation*
Ablation is considered the easiest approach to the third generation of thermal plates, the no-process plates. But interestingly enough some of the announced "processless" plates, are better classified as a sub-group of second generation thermal plates, as they require a processing step in order to arrive at the final image. Either because the provided laser energy is not enough to completely remove the coating in the exposed areas, or because it is desired to hold back the ablated material in a protective overcoat, a processing step will be required. This processing step can either be a wet, aqueous processing step or a dry, wiping step or a wet processing step by the fountain solution on press. Presstek's PEARLGold plate (Presstek – US 5,807,658 and EP 844,080 and EP 825,021) or Anocoils's T-Plate are examples of ablation-based second generation thermal plates.

Tab. 3: Generation II / Sub-Group 4 – Ablation-based second generation thermal plate technology

Presstek	US 5,807,658 EP 844,080 EP 825,021	IR-absorbing layer (Ti) – TiN hydrophilic layer – water-soluble overcoat of PEG
Agfa	EP 683,728	Hardened hydrophilic surface layer – IR absorber

Generation III Thermal Plates
Completely process-free plates ("expose – go to press") are perceived as the Holy Grail, a printer's dream. Since the early days of lasers, researchers have explored the options reaching the Holy Grail by combining new plate formulations with the newly available tool of laser exposure (Hoechst – US 4,063,949, Xerox – US 4,081,572). IR lasers and thermal plate technology seemed to finally push open the door towards processless plates. Again as

processless plates can be and will be based on many different mechanisms; we try to classify them by sub-groups.

Sub-Group 1: Based on *Ablation*
As the laser exposure has to provide all the energy necessary to form the final image, ablative plates typically require rather high exposures. Using thermally unstable or self-oxidizing polymers (e.g. nitrocellulose) in the plate formulation is one approach to bring exposure down, more affordable high power lasers is another way. As ablative systems are based on the rapid thermal decomposition, evaporation or volatilization of the coating, gaseous as well as particulate matter is the by-product, which needs to be collected in the imaging device during the imaging process. The following table gives a short overview of ablative plate technology.

Tab. 4: Generation III / Sub-Group 1 – Ablative plates

Agfa	EP 628,409 WO98/55330 US 5,401,611	Ablation of metallic Ag layer (from DR)
Mitsubishi Paper	DE 19 748 711	Ablation of metallic Ag layer (from DTR)
Kodak	US 5,605,780 US 5,691,114	Ablation of poly-Cyanoacrylate
Polychrome	WO97/00735	Ablation of polypyrroles, polythiophenes, polyanilines
DuPont	US 4,054,094	Ablation of hydrophilic silicic acid layer
Gerber	EP 882,582	Ablation of ink receptive (silver) layer

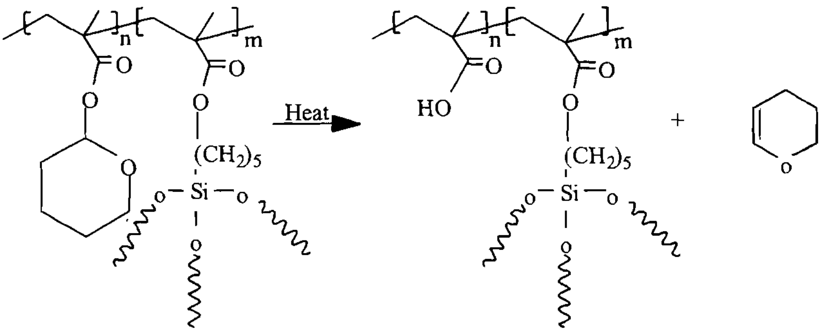
Kodak Polychrome's Navajo plate or DuPont's Silverlith ZP plate are examples of generation III plates, which were shown at tradeshows.

Sub-Group 2: Based on *"Switching"*
"Switching " in the context of irreversibly changing a hydrophilic surface imagewise to an oleophilic surface or vice versa has become an industry buzzword, with a very ill defined technical background.
Some so-called "switchable polymer systems" are better classified as generation II-type plates, as they require a wet processing step, which is accomplished by the fountain solution on-press. The challenge is to find a polymer system which is stable at room temperature for at least 4 – 6 months, but switches at laser temperature (> 600°C) within 10 microseconds. Possible modes of "switching":

- Masking / de-masking of a polar group

A classic example for a positive working plate is the IR dye sensitized acid generation and subsequent acid catalyzed cleavage of acid-labile group pendant from a polymer backbone as described in 3M patents (WO92/09934 and EP 652,483).

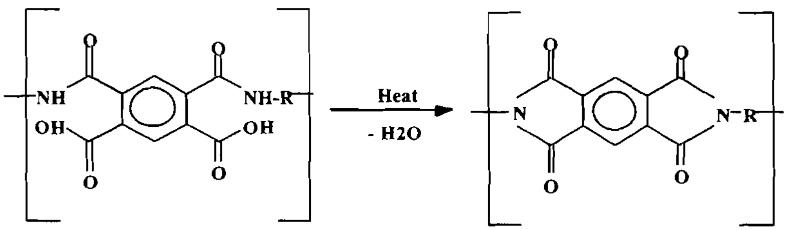
Figure 4: Acid-catalyzed cleavage (3M technology)



3M Patent

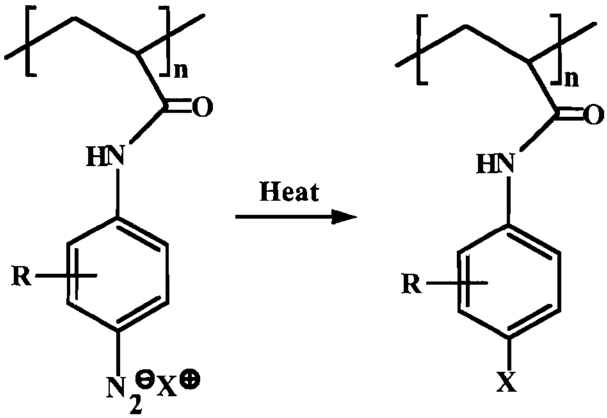
An example for negative working plate is the thermal cyclodehydration of polyamic acids with hydrazide groups as described in Xerox's patent US 4,081,572.

Figure 5: Thermal cyclodehydration (Xerox patent)



destruction / generation of charge
Various examples to negative working plates are described in IBM's patent EP 200,488. All of these examples would fall in a generation II develop-on-press type if the hydrophilic starting polymers were not properly crosslinked to the substrate.

Figure 6: Charge Destruction (IBM patent)



IBM Patent

- Physical change plus chemical reaction (coalescence; rupture of microcapsules)

Various examples based on thermal coalescence of hydrophobic (thermoplastic polymer) particles dispersed in a hydrophilic binder (Agfa – EP 770,494, EP 770,495, EP 770,497, EP 773,112, EP 773,13, EP 774,364, EP 849,090) are described in the literature. Another example based on the thermally induced rupture of microcapsules and the subsequent reaction of the microencapsulated oleophilic materials (isocyanates) with functional (hydroxyl-) groups on crosslinked hydrophilic binders is described in the literature (Asahi – US 5,569,573, EP 646,476, WO94/2395, WO98/29258), and has been demonstrated at IPEX 98.

A potential 2-layer approach to a "switchable" system is described by Fuji (JP 10069089), imagewise crosslinking a water-soluble bottom layer with a phenolic top layer.

Our own developmental work on "switchable polymers" is strongly supported by analytical as well as theoretical studies (thermal gravimetric analysis, isothermal IR, temperature ramped MS or pyrolysis GC/MS, Arrhenius studies, reflectance IR of the imaged plates, SEM of imaged and non-imaged plate areas). Emissions are a general concern with these non-ablative, processless generation III systems. As much as everybody would like to see water or carbon dioxide as the only emissions, the 3M patent clearly reveals that we have to be prepared to handle much "nastier" emissions. Further, if the starting hydrophilic polymers are not properly adhered to the substrate we will end up with generation II type develop-on-press systems. For truly non-ablative generation III type thermal plates good wear behavior / run length will be a challenge.

Thermal Digital Waterless Printing Plate Technologies

In contrast to the conventionally printing world, there has NOT been a first generation thermal technology plate development. The explanation is straightforward. All current waterless plates rely on silicone technology for the non-image areas. This implies the need for two layer concepts. (Admittedly, it is scientifically possible to design silicone resins to effect a single-layer thermal waterless plate, we'll discuss this later, but it is still very difficult in practice). Therefore, the earliest thermal waterless plate concepts involve either the need for chemical processing or are ablative technologies that require a mechanical wash-up step. Since the latter were the first commercial digital waterless plates on the market we'll discuss them first.

Thermally ablative waterless plates are characterized by a multiple layer design, typically consisting of a substrate (either polyester or aluminum), an oleophilic (ink-adhesive) layer, an IR sensitive layer, and a (ink repellent = ink abhesive) silicone topcoat. The principle involves the transparency of the silicone layer to IR, the thermal insulation provided by both the silicone above and the oleophilic layer below the IR absorbing layer and the ablation caused by intense thermal spike caused by IR absorption. As described by Lewis (1996) in US 5,487,338 such a possible waterless plate on polyester might comprise:

A first durable, oleophobic polymer layer (silicone) which includes IR absorbing material.

A solid oleophilic substrate underlying the first layer (polyester containing a dispersed pigment to reflecting imaging radiation)

A layer of IR-absorptive metal oxide (titanium oxide) disposed above the substrate.

Fundamental studies by Hare, et al. (1997) have shown that the ablated materials tend to emit as chunks of matter directly back from the direction of the thermal input. Due to a combination of factors, the emitted materials do not completely escape from the vicinity of the plate surface. These plates require a mechanical cleaning, usually with a mild solvent to effect a quicker removal of the ablated matter from the plate surface prior to printing.

A variation on thermally ablative waterless plate technology would utilize the concept of explosive ablation to cause the materials to emit from the plate surface to have a trajectory that did not intersect the plate surface; the ablated materials could be captured by suitable vacuum designs built into the platesetter. The prototype of this technology announced by Kodak at Print 97 consisted of two layers on polyester (PET) or aluminum; the topcoat an IR absorbing proprietary silicone composition, the second coat an IR absorbing, oleophilic layer directly onto PET or aluminum. Ink acceptance in the image areas ("write the image") was the result of full ablation of the oleophobic silicone toplayer as well as partial ablation of the oleophilic, IR absorbing layer that incorporates organic resins. This technology which reached feasibility stage has not been commercialized due to the high thermal energies which would be needed to effect full exposure, without the need for a mechanical wiping step prior to printing, in a plate construction with the requested run length of 25,000 impressions.

Another "second generation" thermal waterless plate technology, that is, no preheat, involves the use of chemical (and mechanical processing post-exposure) development. These plates are also two layers on aluminum. The topcoat is proprietary silicone; the second coat is IR absorbing, resin containing, directly on aluminum. There are two prototype products currently in limited release; the Toray Emerald and the Kodak Polychrome NAW. Fuji (1999) has obtained a patent for a similar concept (US 5,849,464) but has not offered a plate to the market.

In one example of this concept an ink abhesive layer is applied between the IR absorbing layer and aluminum substrate. Upon development of the laser-struck areas the oleophilic organic layer is revealed. The NAW is developed completely removing both the silicone and IR absorbing layers from laser-struck areas revealing the underlying aluminum as the ink abhesive layer. Both concepts show the high thermal efficiency characteristic of non-preheat chemically developed technologies.

There is not today any examples corresponding to a third generation thermal waterless plate technology. That is, a plate which can be mounted on press (or exposed on press) without some mechanical assist. However, the Pearl Dry Plus plate from Presstek advertises a dramatically reduced mechanical requirement relative to their Pearl Dry technology, ie a short duration water wash instead of a longer solvent wipe. There is no indication this Pearl Dry Plus represents dramatically new technology, however.

The Holy Grail

The particular importance of the generations of thermal plate technologies is not merely to report a technological story. The crucial observation is that thermal plate technology developments are proceeding towards the printers' Holy Grail. The Holy Grail is a printing plate mechanism whereby a plate is imaged without any processing required which runs with a "single fluid" inking system preset by the digital imaging files. There is some controversy whether the Holy Grail includes "on-press" imaging or "off-press, instant loading" imaging technology. And also whether the "single fluid" is a premixed precision pre-emulsified ink/fountain combination or "waterless ink", as we know it. Clearly, technology convergence towards the Holy Grail must also consider the necessary energy input requirements, required run lengths per plate and rewritability or reusability of the plate substrates. Nevertheless, thermal plate technology is developments are strongly encouraging; the Holy Grail should be "in hand" during this generation's planning horizon.

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