A New Photopolymer Technology for a Develop-On-Press, Thermal CTP Plate

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Abstract

Immediately following the successful introduction of Thermal CTP, attention turned to the promise of "Processless" CTP plates. Removal of the developer and the processor from the pre-press area would provide welcome cost, time and space benefits to printers. Many iterations of technology have been attempted in laboratories and also in the market. However, until recently no single technology has successfully delivered a commercial, "processless" plate with these customer benefits.

A new technology will be discussed which has allowed the introduction of the first Thermal CTP plate which requires neither a developer, nor a processor, nor a debris-collecting platesetter, and which still provides a traditional printing background. The plate is a "Develop-On-Press" (DOP) plate. It has presented the plate designer with a new set of challenges; how to prevent press contamination, and how to develop-on-press without increasing make-ready time.

The solution represents a technological advance in the application of photopolymers in litho plates. Polymers will be described which provide a unique chemical effect to allow a novel, single layer coating to be used. This helps to minimize coating weight and reduce contamination. The same polymer also provides a particulate structure, which contributes to excellent developability in fountain solutions.

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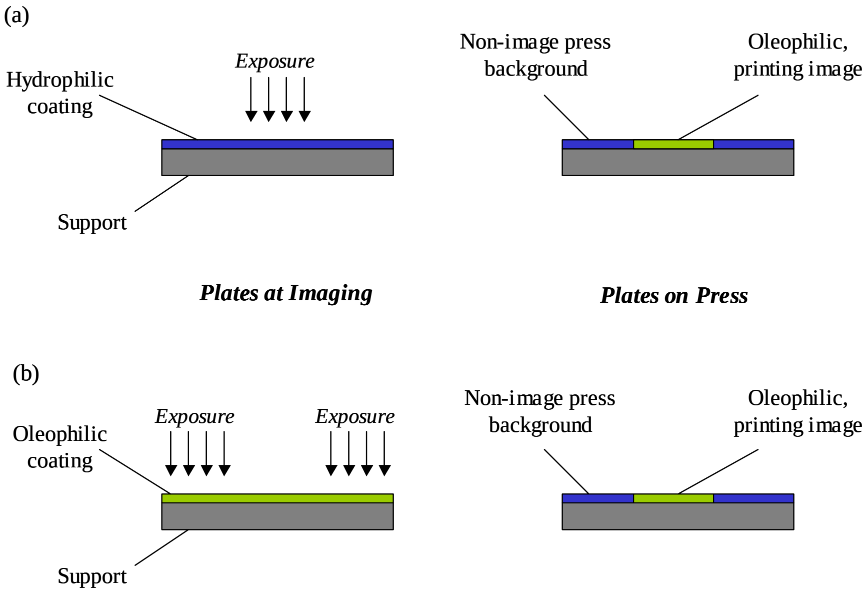
Introduction

Switchable technology and challenges

Many patent applications - and print show technology demos - have described “switchable” polymers; coating layers that switch their ink/water accepting properties simply by exposure. The imaging either switches a hydrophilic, coated layer to oleophilic, figure 1a, or the reverse, figure 1b. This elegant “end-game” for Thermal CTP, just image and print without ablation or processing, has never been successfully commercialized, as the technical barriers are high.

Figure 1: Plate assemblies for switchable polymer litho plates



In a standard wet litho plate, the imaging exposure causes a change in the solubility of an oleophilic layer. The change in solubility allows imagewise removal of the oleophilic layer to reveal the hydrophilic surface of the substrate. The ink/water differentiation of a wet litho plate derives from the different surfaces, which have consistent opposing affinities for ink and water, throughout the process. Therefore, the focus of research work on traditional plates has been to establish a robust, large “solubility differential” in an oleophilic layer.

In a switchable polymer plate, the chemical reactions that occur must change the ink/water affinity of the coating. This “ink/water differential” is as critical to the switchable plate performance as the solubility differential is for wet process plates. Most published technologies use a hydrophilic to oleophilic switch. No solubility differential is necessary, and indeed could be detrimental. Chemical reactions able to switch are very limited and often need high exposure energies, i.e. slow plates, which can then lead to unwanted ablation. Formulation components added to provide chemical and physical robustness for run length and aging stability, typically compromise the magnitude of the ink/water differential!

In summary, a switching reaction is required that has a sufficiently large ink/water differential to provide robustness on press, and all with a competitive imaging speed, and after compromises for other plate features have been introduced! This product has not been delivered to the market and it may be some years off. It is the authors' view that the lack of press robustness is a significant barrier to any successful processless plate introduction and has been a limitation in many developer-free plate systems.

Ablation technology and challenges

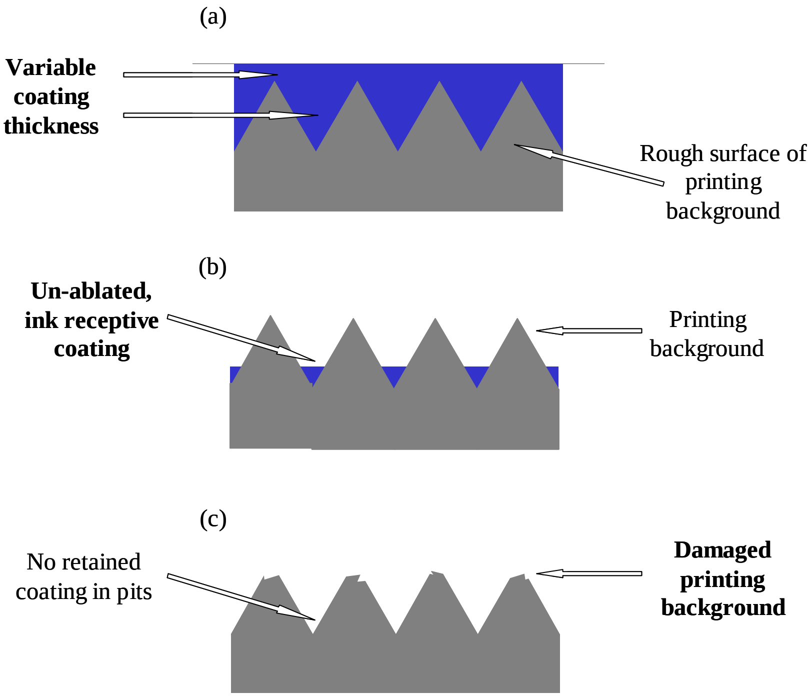
Another technology option discussed from the mid-90's was "ablation". The explosive removal of materials is an obvious starting point when using thermal lasers to generate an image on a plate, without developer or processor. This preference would provide a route to a "processless" plate, without relying on ink/water differential on imaging, and could use a traditional plate background on press.

The plate designer simply provides an oleophilic, ablative coating on a grained, anodized aluminum substrate and ablates away this layer using a laser, revealing the hydrophilic background. Unfortunately, this is not a trivial task. The printing background has a very rough surface on a micro level, with pits up to 10 microns deep and 10 microns diameter. This provides an invaluable boost to water carrying properties. Figure 2a shows that a coating on such a surface is not of a uniform thickness, being thicker in the deep pits, and thinner on the peaks.

Figure 2b illustrates that when sufficient laser power has been used to ablate the thin coating regions, there remains unexposed material in the deep pits – this will not print clean! As energy is increased to clean out the pit material, the exposed peaks of the substrate are damaged by the exposure, figure 2c. The pressroom sees a compromise in plate background performance, and low platesetter productivity in prepress. To date it has not been possible to provide an ablative coating on a traditional substrate to yield a robust printing plate.

Attempts to invert the layers, i.e. ablate away the hydrophilic layer to reveal the oleophilic image, have been considered. In such a system, the hydrophilic

Figure 2: Challenges of ablation



printing background can no longer be the traditional, grained, anodized aluminum. The plate designer has to provide a coatable, hydrophilic uppermost layer, which could be removed by ablation. This is as yet, an unsolved challenge.

Other attempted commercial solutions involve “partial ablation”. A loosened, imaged coating is cleaned out by processing off-press to reveal the background – but the processor is back!!

The ***common constraint*** for both switchable and ablative systems, is that there has never been a broad market acceptance of a wet litho plate having a ***non-standard printing background***. The unique hydrophilic and very tough nature of the anodized aluminum surface, with the additional surface volume from the graining, has yet to be mimicked in a coated layer!

The requirement for wet processing on the press

It is clear from previous attempts that robust press performance can only be achieved using the traditional, grained, anodized aluminum. The only way to get this wonderful surface performing on a press cylinder, is to wash off areas of oleophilic coating from a pre-sensitized plate. This says the processing step is a pre-requisite for a plate system with excellent printing.

There are two opportunities for wet development: off press in a processor, or on press with the aqueous solutions, and/or ink, used in the printing process, i.e. ***Develop-On-Press (DOP)***. The latter option provides a route to removing the processor and special development chemistries from the pre-press room.

The authors believe that the press must be used as a processor, when processless plates are desired. This adds a number of design constraints for the plate designer, required to satisfy the demands of the printer:

- the removed coating cannot affect press performance.
- the development process cannot reduce profitability.
    - No increase in paper waste
    - No increase in press down time

Press robustness and the exposure differential

In a positive working (write-the-background), wet processed plate the coated layer must (a) be insoluble in the processing system, and (b) have sufficient physical and chemical robustness to provide good run length and scratch resistance. Figure 3 shows the unexposed coating has an inherent resistance to abrasion and chemical attack, and is insoluble. On exposure there must be sufficient increase in solubility so exposed areas are developable, the "exposure differential". Each plate technology has an inherent exposure differential, the larger the better! The differential can usefully be amplified through control of physical development methods, including brush choice, developer temperature, residence time and also developer selection. The inherent solubility is not actually increased using the processor and developer, but the apparent solubility is improved so no increase in exposure differential is required. This total "processed differential" provides the final, robust system for the user. The exposure differential does not have to achieve everything on its own.

It is possible to increase the exposure differential simply by increasing the imaging energy, but there are limitations. Increasing imaging energy is not without consequences and will negatively impact platesetter productivity, which for many customers is unacceptable. An alternative is to increase the intrinsic exposure differential of the coating. This means increased efficiency of the chemical reactions, which occur on exposure. The compromise here is the shelf-

Figure 3: Schematic of positive working exposure and processed differentials

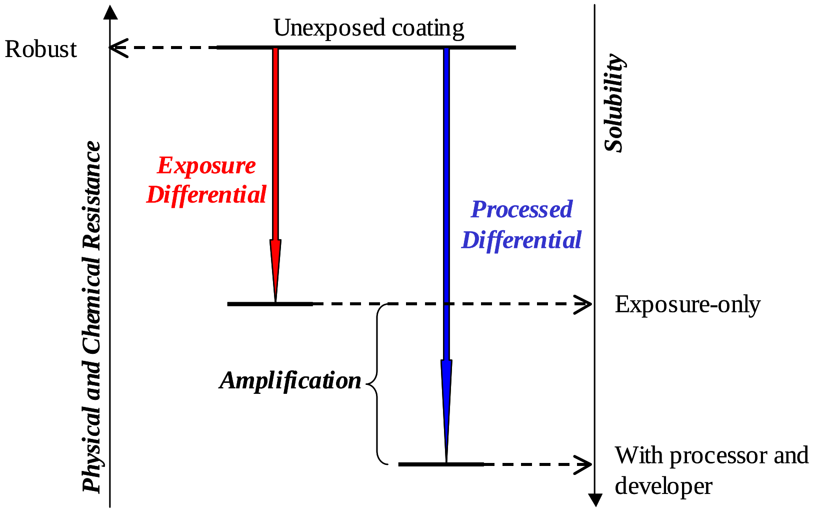
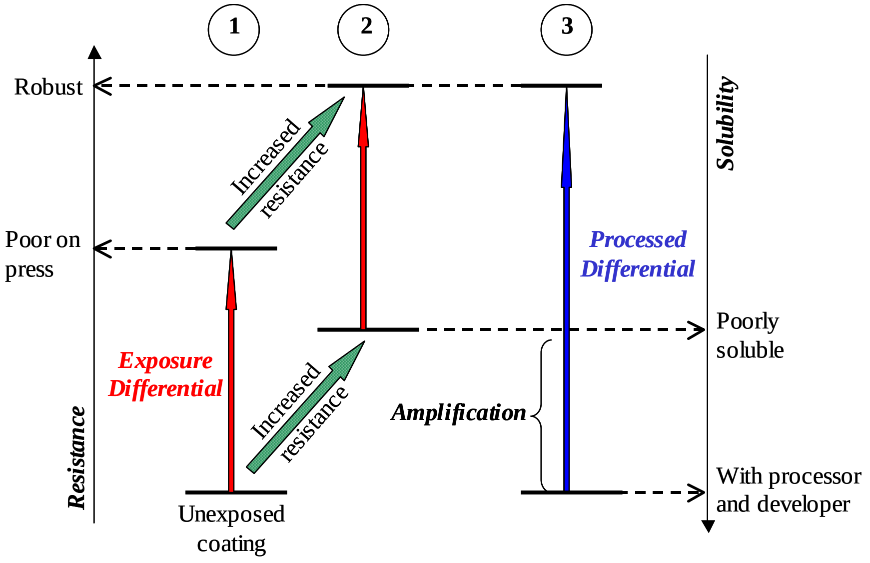


Figure 4: Schematic of negative working exposure and processed differentials



life of the plate. As “more efficient” is essentially “less stable”, long term stability of the plate will be decreased.

The requirements for exposure and processed differential are reversed for a negative working plate. The non-image areas are soluble in the processing system and the exposure, this time, is required to harden the coating to print robustly on press, figure 4-1. If the intrinsic exposure differential is insufficient, the system needs to be optimized to allow amplification to be effective.

The plate designer requires an increase in resistance of the unexposed coating, which provides the corresponding increase in the robustness of the image on press, figure 4-2. Now processor and developer amplification methods can be employed to increase the processed differential to provide the required system performance, figure 4-3.

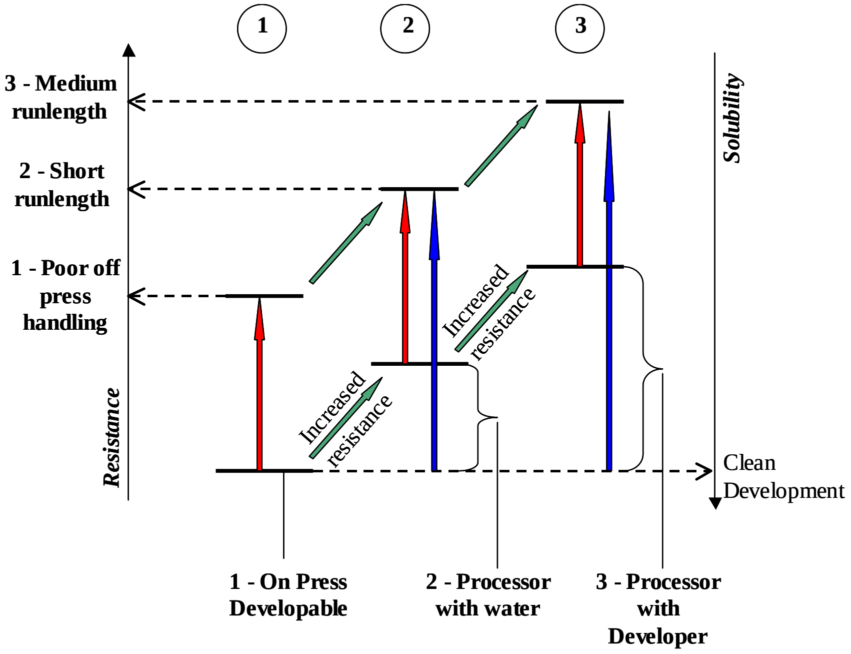
A consequence of the use of a processor and developer can be damage to the plate background, and in some instances, the gumming step becomes a requirement to “repair” the background and ensure a trouble free press start-up. It is interesting to note that gums – applied at coating weights of the same order of the DOP plates to be discussed here - are routinely washed off, into the printing units of almost all presses in the world, without effect of contamination!

Methods to maximize processed differential, are used then, to optimal effect in off-press processed plates. These methods, however, cannot be used as a design principle for a DOP plate, when the processor is the press. Brushes cannot replace ink/water forms, the fount train can’t be heated to elevated temperatures and it is not practical to force a printer to change his press chemicals!

Technology choice to maximize exposure differential

It is critical then to make an advantageous technology choice to maximize exposure differential, without which, DOP is not feasible. For example, a negative working technology, which has a limited, intrinsic exposure differential can be made to be developable on press by designing the unexposed solubility to a suitable level, figure 5-1. However, if the exposure differential is insufficient, the coating will not be resistant enough for off-press handling or run length. In order to increase the suitability for good press performance, the exposed <u>and</u> unexposed solubility would have to be increased. Then to use the plate, amplification would be required for clean development. A coating that is primarily fount soluble might be processed using water in an off-press processor, providing greater physical action than possible on the press, figure 5-2. This way a plate, suitable for off-press imaging and short runs, is possible. Additional increases in run lengths can be accomplished by increasing robustness of the unexposed coating, but only if, further processed amplification were provided. For example, adding specific chemicals into the processor would aid clean out of the more resistant, unexposed coating, figure 5-3.

Figure 5: Product progression when limited to low exposure differential



The solubility adjustments employed, mean that the unexposed coating is no longer sufficiently soluble for a DOP plate. The compromises (selected to provide an increase over exposure differential) to make the plate run on press, simply move the product further away from a true processless plate offering and remove the many benefits of the "processless" promise.

Is it possible to provide an improved exposure differential for robust off-press handling and on-press running, or can an alternate strategy for amplification be applied?

Photopolymer Technology

For years, digital negative working (write-the-image) plates have demonstrated faster imaging speeds than the positive working counterparts, the fastest of these being photopolymer plates. They achieve the speed by use of a chain reaction, which allows for multiple crosslinking reactions resulting from a single photon of energy being absorbed by the coating. Such chain reactions are not present in commonly exploited thermal-only mechanisms such as: reversible insolubilization, e.g. KODAK ELECTRA Excel; physical insolubilization, e.g. KODAK SWORD Excel; or thermal coalescence, e.g. Agfa's Azura. The photopolymer chain reaction has proven critical in maximizing the intrinsic exposure differential for the Thermal Direct plate technology.

Photopolymer technology, has, traditionally required two features that are unacceptable in a DOP plate: a) a thick overcoat of a polyvinyl alcohol that is used to form a barrier to atmospheric oxygen, which would otherwise quench the chain reactions before they were able to produce useful work, and (b) a heating step prior to development. For example, the KODAK THERMAL NEWS plate is imaged at 120 mJ/cm^2, but expose the photosensitive layer without its topcoat and there will be no image after processing! These layers can double the film weight of the total plate, and comprise resins that would contaminate a press.

The second undesirable feature, the heating step, forces the chain reaction of a photopolymer plate to completion, providing a significant boost to the exposure differential of the plate. If the pre-heat process is omitted, the drop in imaging speed is severe, and no printable image is generated. It is not possible to apply a pre-heat prior to development on press without compromising the benefits of a DOP plate, i.e. no pre-press equipment!

Key to all photopolymer systems is the initiator and sensitizer combination, which together absorb the imaging energy, and start the chain reaction in the coating. Much effort has been spent in optimizing the selection and the Thermal Direct plate uses an iodonium salt and an IR dye having an anionic chromophore. Even though optimized, without the topcoat and pre-heat, the imaging speed of Thermal Direct is still limited in comparison to a plate system such as Thermal News.

Chemical resistance as an alternate amplification process

A new "trick" is invoked in the design of Thermal Direct to provide an alternate amplification step in the absence of a developer or processor. As stated above, there are two contributions to image layer robustness on press: physical and chemical resistance. Physical resistance comes primarily from the crosslinked polymer network, which provides the exposure differential. Chemical resistance comes both from the crosslinking and the chemical structure of the materials used.

The materials used in Thermal Direct have been specifically designed to provide a very high level of press chemical resistance, without compromising other desired properties, such as developability. The important monomer introduced in to the polymer is acrylonitrile (AN). This monomer has been demonstrated to provide an increase in chemical resistance to solvents used in common press chemicals, without an increase in developability of the unexposed coating. Figure 6 illustrates that the introduction of this functional group provides an additional increase in the robustness of the plate on press, over the exposure differential; a “chemical differential”.

Figure 6: Schematic to show chemical differential in Thermal Direct

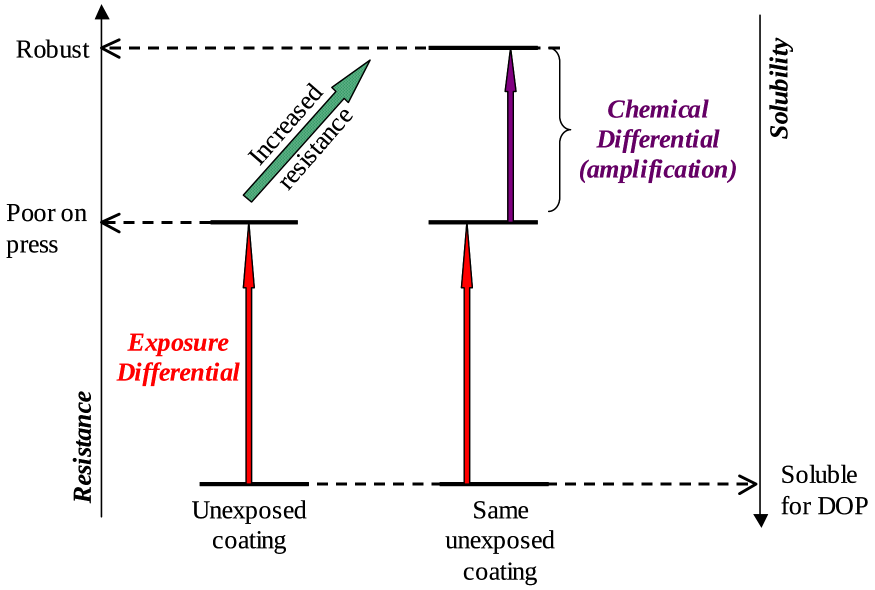


Table 1 shows the benefits of these polymers on the run length and chemical resistance of a DOP plate. The AN-containing polymers, B and C, do not have any additional crosslinking capability compared to the reference polymer, A, showing that the run length increase is coming solely from the inherent chemical resistance provided. These AN-containing polymers also allow the coating film weight to be kept at a minimum for a given run length, to reduce press contamination concerns.

Table 1: Runlength and Chemical resistance of DOP plates using AN-containing polymer

Polymer	Copolymer Composition / wt%			Press Evaluation	
	PEGMA[1]	ST[2]	**AN[3]**	Run length[4]	V-120 test[5]
A	10	90	**0**	**16,000**	**Image areas removed**
B	10	13	**77**	**>45,000**	**No effect**
C	10	20	**70**	**>40,000**	**No effect**

Notes

1. Poly(ethylene glycol) methacrylate
2. Styrene
3. Acrylonitrile
4. Plates imaged on a Trendsetter 3244 at 250 mJ/cm^2 and then mounted directly on Komori Sprint 26 printing press, Graphic Equinox black ink, Varn Litho Etch 142W (3 oz/gal) PAR alcohol replacement (3 oz/gal).
5. V-120 press wash (Varn International), applied to image areas for 1 minute after 5000 impressions.

One significant advantage of increasing the differential in this way is that there is no effect on shelf-life of the system. The introduction of acrylonitrile into the polymers does not affect the efficiency of the imaging reactions themselves. Therefore, there is no decrease in stability of the plate.

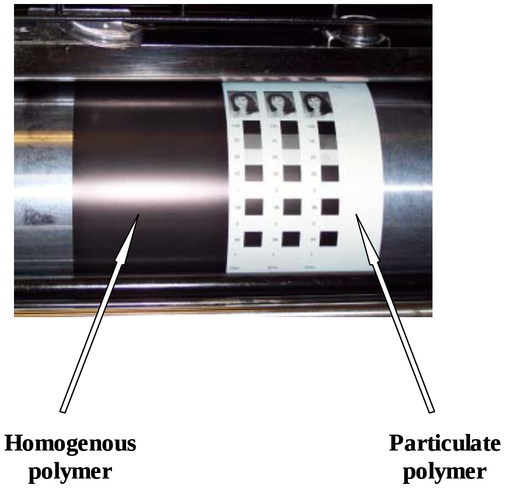
Using the photopolymer technology optimized for exposure differential, and the new binders to provide additional amplification of the differential, the next design features unique to DOP can be approached: providing a coating that has sufficient solubility to be removed from the printing background within the bounds of all current litho print process and ensuring that this removed coating does not affect the press adversely.

Polymers for fast make ready and zero press contamination

The traditional method for providing increased solubility is to introduce water-soluble functional groups within the polymer of the plate, such as carboxylic acid and methacrylate groups - though this approach can be limited. The polymer is also required to provide other plate features, for example, ink receptivity, and functional groups having an inherent affinity for water compromise ink receptivity.

One of the important inventions introduced in the Kodak DOP technology is the use of a particulate polymer within the coating. The particulate form of the polymer shows a significantly improved developability on the press. Figure 7 shows the same solids formulation coated in two ways, the first with the polymer homogenously dispersed throughout the coating and in the second, the polymer is particulate. The homogeneous system has not developed after the standard start-up procedure and 10 impressions - the difference is dramatic! This invention has allowed our material designers scope to provide an excellent balance of ink receptivity, reactivity and solubility.

Figure 7: Contribution of particulate polymer to on press development



There is a range of preferred particle sizes for the polymers in Thermal Direct. If the particle size is too small there is only a correspondingly small improvement in developability. Increasing the particle size increases the solubility of the polymer, however, as should be expected, if the solubility is increased too far then the exposure differential will no longer be sufficient to provide a robust printing imaged. Table 2 shows the increasing rate of development with increasing particle size, up to a level at which the imaged coating has begun to show rapid wear.

Table 2: Effect of polymer particle size on developability

Polymer	Median Particle diameter[1] / nm	Impressions to Clean Background [2]
D	60	>200
E	180	<10
F	256	<5
G	800	<5 Imaged areas worn after 150 imp.

Notes

1. Microtrac UPA150 particle size analyzer.
2. Plates imaged on a Trendsetter 3244 at 240 $mJcm^{-2}$ and then mounted directly on an AB Dick 9870 Offset Duplicator without further processing. The press was charged with Van Son Rubber Base Black 10850 ink and fountain solution containing Varn Litho Etch 142 W(3 oz/gal) PAR alcohol replacement (3 oz/gal).

Once the benefits of the particulate nature of the polymer had been identified, work to optimize the chemical structure of the polymer for solubility, could begin. Unusually, with the particulate form of the polymer, the traditional solubilizing functional groups were not required. It was found, however, that the use of poly (ethylene glycol) side chains from an acrylic backbone did provide a route to fine tuning developability.

Tables 3 and 4 illustrate the different contributions to developability of the physical and chemical nature of the polymer. Polymer H has a level of the traditional solubilizing group, methacrylic acid, but is not in a particulate form. Polymer I has no methacrylic acid, but instead contains poly (ethylene glycol) methacrylate (PEGMA) and is in particulate form. Plate 1, comprising only Polymer H, takes far longer to develop on press than Plate 2, where Polymer I has been substituted into the formulation.

Plate 3, using Polymer J with 100% methyl methacrylate, is in particulate form as Polymer I, yet is still slower to develop than Plate 2.

Table 3: Polymers with varying functional groups and particulate nature

Polymer	Copolymer Composition / wt%				Particulate?
	Methacrylic acid	Styrene	PEGMA	Methyl methacrylate	
H	13	87	-		✗
I	-	90.5	9.5		✓
J	-	-	-	100	✓

Table 4: Effect of physical and chemical structure of the polymer on development

Plate	Polymer ratios / wt%			Impressions to Clean Background [1]
	Polymer H	Polymer I	Polymer J	
1	100	0	0	>>200
2	20	80	0	<5
3	0	0	100	>200

Notes

1. Plates imaged on a Trendsetter 3244 at 240 mJ/cm^2 and then mounted directly on an AB Dick 9870 Offset Duplicator without further processing. The press was charged with Van Son Rubber Base Black 10850 ink and fountain solution containing Varn Litho Etch 142 W(3 oz/gal) PAR alcohol replacement (3 oz/gal).

The combination of the two methods to boost solubility provides an additional benefit – shelf-life stability. The failure mode on aging of these DOP plates is a reduction in developability, resulting in more sheets to clean the background fully. Starting with an excellent solubility level has allowed the Thermal Direct plate to achieve a minimum 18 months shelf-life without affecting plate performance.

The recommended start-up procedure for KODAK THERMAL DIRECT on press is to run for 10 - 20 revolutions (depending on the press) with the dampening rollers engaged during which time the coating begins to swell and solubilize. Next, the ink rollers are engaged for a further 10 - 20 revolutions during which time the tack of the ink adds a physical dimension to the development. The press is then put on impression and the unwanted coating is removed on the first several make-ready sheets.

The solubility provided by the physical and chemical structure of the Thermal Direct polymers has been successful in satisfying the unique demands of DOP. No special presses are required, neither are special ink and fount combinations and all this without any additional impact on press downtime or yield. Finally, there have not been press contamination issues in any customer - with Thermal Direct's longest running customer now using 100% DOP for over 1½ years.

Dot measurements - an intrinsic constraint of processless

If the background is not fully developed to reveal the printing dots prior to mounting on press, it is not possible to use a densitometer to measure the dots.
A recent Seybold Report article dealt with the practicalities of this for the printer, and indeed concluded that DOP may not be for everyone.

The minimum required is an exposure contrast that is readable to ensure the correct plates are placed on their respective press units. For the plate designer this has provided one final challenge. The coating that is removed from the plate cannot affect the ink colors on press and so needs to have no color itself. The final exposed image color has to be generated from a colorless background using the same imaging energy used to provide the insolubilizing reaction. This competition for energy between color change and solubilization/insolubilization has been a challenge for all plate designs for many years, this is accentuated in DOP as the normal amplification methods, to increase exposure differential, cannot be used.

The color system in Thermal Direct relies on a unique property of the selected IR dye. Degradation, on exposure of the IR dye, results in the color change, and it has not been necessary to include additional color change promoters, which can add further complications in formulation. The color change has proved sufficient in all customer sites for correct placement of plates on press units and the DOP robustness has provided no problems with consistency of printed dots.

As the Seybold report concludes, if a customer finds it essential to read the dots on the plate, be prepared to make space for the processor. If this is the right route for the customer, then consider using a full developer system, not simply water (the processor will be on the floor either way). As this paper describes, the most robust plate, with the fastest imaging, is provided when both processor and developer amplification is used.

Conclusion

The wet development process is shown to be necessary to provide the robust background non-printing surface, a pillar of the litho print process. Development-on-press is offered as a route to provide wet development without the requirement for processing equipment or chemistry. However, this demands a new set of performance criteria from the lithographic coating. The solution presented here represents a technological advance in the application of photopolymer technology for litho plates. Technology selection and polymer structure has enabled a robust exposure and print performance to be achieved. Unique physical structure of the polymers provides a route for excellent developability and zero press contamination. The first commercialized product using this technology, KODAK THERMAL DIRECT, offers the first litho plate with no compromise of the “processless” promise – no developer, no processor, no effect on press performance.

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