New Generation of NPH, Thermal CTP Plates

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Abstract

The mechanism of commercial, positive-working, thermal CTP plates is based on physical insolubilization within a single layer between a polymer and an insolubilizer. Rapid heating on exposure causes the insoluble, hydrogen-bonded structure to break and solubility in a high pH developer is restored. Fast imaging speeds are achieved, but shelf life is limited. Crucially, the plates have limited resistance to aggressive blanket wash, plate cleaning agents and alcohol substitutes in fountain water.

Attempts to improve solvent resistance by modification of the polymers, or addition of alternative polymers, will fail. Resulting plates have neither blanket wash resistance nor fast imaging speed.

We will discuss a new generation of CTP plates where solvent resistance and fast imaging speed are obtained through use of distinct layers. This two-layer, physical deformation mechanism also demonstrates excellent shelf life, and development can be tailored through material choice for either high or low pH developers.

Introduction

In 1995, the first Thermal CTP plate was introduced, and is still on the market today, the Kodak Polychrome Graphics Thermal Printing Plate/830. The combination of this plate with the Creo Platesetter drove a significant shift to Thermal from the Visible light systems that were on the market that time. For the printer this combination gave the advantages of CTP in pre-press but with conventional on-press performance, including the ability to post bake the plate for long runs.

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This was achieved through use of phenolic resins, which have formed the backbone of conventional positive plates for the past 30 years. The mechanism utilizes IR dye sensitized acid generation, followed by heating to complete acid catalyzed crosslinking of the resin and a resole. On development, this system produces a negative, write-the-image plate. The compromise for the printer was a large oven in the pre-press area for the heating step prior to development. However, for the early adopters of CTP, space and capital was a small price to pay for CTP and the future of Thermal CTP was rapidly secured with this Pre-Heat (PH) plate.

The challenge for plate designers was then to remove this pre-heat oven from the system. 1997 saw the introduction of the first No Pre-Heat (NPH) Thermal CTP plate, Kodak Polychrome Graphics Electra 830, which utilized a physical insolubilization mechanism.

By the close of 2004, NPH plates based on physical insolubilization accounted for approximately 70 million m^2 of the 200 million m^2 CTP plates sold in the worldwide market. In comparison, the PH plates derived from the original Kodak design accounted for approximately 25 million m^2 of worldwide CTP. With a ratio of close to 3:1 NPH to PH Thermal, the physical insolubilization based plates clearly have been extremely successful, and as new installs are almost 100% NPH this ratio is only increasing. So why was there a need for an additional NPH mechanism?

When the plate volumes of NPH and PH are broken down regionally, the primary reason becomes clear. In the US, PH plate volume far exceeded the volume of NPH plates in the market. Kodak Polychrome Graphics (KPG) struggled to make an impact with Electra 830, or its successor Kodak Polychrome Graphics Electra Excel, unless the product was post-baked, and instead chose to lead with the PH type plates. The Achilles heel of the physical insolubilization NPH plates has been poor unbaked runlength in US press rooms.

The US uses alcohol substitute founts extensively and the organic solvents in these solutions are very aggressive towards the coatings of the NPH plates, when they are not post-baked. This same failure in runlength is not the case using the PH CTP plates without post-baking. In Europe, Japan, Asia and parts of Latin America, growth of the NPH plates has far exceeded PH plates as conventional alcohol founts are still used extensively on press, since they do not adversely affect runlength of the non post-baked plates.

A secondary driver is the desire to have a CTP plate that could be used in other chemically aggressive press environments without the need for post-baking, UV print applications for example.

Physical insolubilization NPH - mechanism and limitations

As stated above, the mechanism of the first NPH plate, and of its successor and competitors, is physical insolubilization. These plates take advantage of the intrinsic secondary structure of novolak resins provided by inter- and intra-molecular hydrogen bonding. This structure inhibits resin dissolution but can be reversed by heating to give a solubility differential on imagewise thermal exposure. Addition of other inhibitor molecules can further increase the solubility differential, and make a usable plate.

Typical formulations suitable for such plates appear very simple, as individual components contribute multiple functions in the composition. For example, the novolak resin provides the key component of the solubility switch, the printing image and the capability of baking for long runs.

However, these systems require a fine balance precisely because the key plate properties, e.g. imaging speed, processing latitude and scratch resistance, are each affected by materials with multiple functions. Change one and you can affect one or more of the other responses.

The manufacture process also became more difficult, compared to conventional plates and the PH CTP plates, in order to produce a suitably stable formulation. The composition does not reach a stable state on drying and initial formulations were found to have very poor shelf life, seen as a slowing of imaging speed, after initial coating. The solution is to accelerate the structure building within the manufacturing process so no instability is then observed through the subsequent supply chain to the customer.

The first commercial NPH plate went through an elevated temperature treatment in order to push structure to completion, a so-called "conditioning" process. This could be simply viewed as taking the oven compromise out of the customer shop and placing the oven compromise at the plate manufacturer. More than 50% of the volume supplied worldwide now passes through an elevated temperature treatment.

So why didn't the new, novolak based, NPH plates not perform comparably to the PH plates in the US? This is due to the difference in the insolubilization mechanism of the novolaks. In the PH systems, actual chemical crosslinks are generated whereas in the NPH plates these are reversible hydrogen bonds. Clearly the former is far more robust to chemical attack in the pressroom if unbaked.

The challenge then for physical insolubilization plates is to increase the chemical resistance of the coatings to compensate for the lack of chemical

crosslinks, without compromising an already finely balanced system performance. There are three routes which have been attempted:

i) *Modification of the phenolic resin*: there are few options to provide a significant boost in solvent resistance for a single, or blended, phenolic resin layer. Molecular weight increases for example only provide a small improvement in resistance to alcohol substitute founts, but imaging speed and resolution are unacceptably compromised.

ii) *Addition of solvent resistant resin to a phenolic composition*: Some improvements in resistance to alcohol substitute founts can be achieved by blending with non-phenolic polymers, for example, sulfonamide type resins (figure 1). However, this is not without compromises. The novolak reduces the solvent resistance of the acrylic resin, and the acrylic resin reduces the developer latitude of the novolak. It has not been possible to use the blending approach to achieve a robust plate with sufficient resistance for use in UV printing applications.

Figure 1: an example of a sulfonamide type resin for solvent resistance

all monomers at least 10 mol%
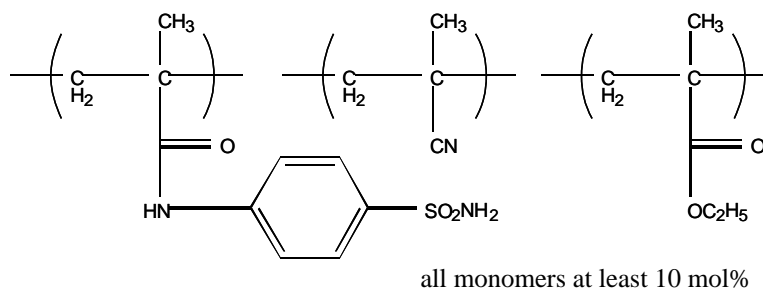
iii) *Use of a novel inhibiting resin with intrinsic solvent resistance*: To substitute the phenolic in this mechanism is a very difficult task. The secondary structure in the phenolic layer is key to amplifying the solubility differential to provide good imaging speed with robust processing. This structural feature is hard to replace with an acrylic type resin and attempts result in slower imaging speed if processing robustness is maintained. An example is shown in figure 2.

Figure 2: an example of a novel inhibiting resin with solvent resistance
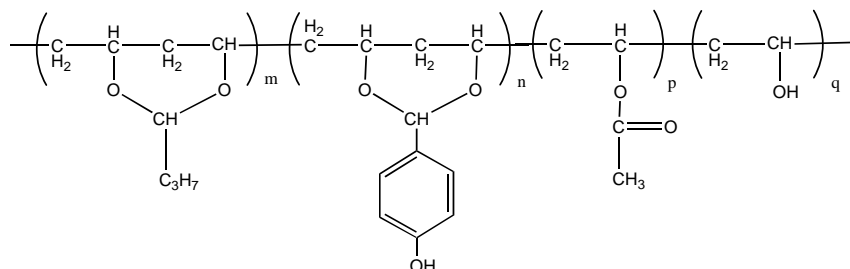
m = 5 to 40%, n = 5 to 60%, p = 2 to 20%, q = 5 to 50%

NPH plates based on physical insolubilization remain challenged when used without post-baking in chemically resistant pressrooms.

A new solvent resistant NPH plate

In order to provide a true, unbaked, solvent resistant NPH plate an alternate mechanism was required in order to break the constraints of the physical insolubilized system. The obvious approach was to attempt to split up the various functions of the multi-purpose materials, ultimately this extended to placing the materials into separate layers of the plate assembly.

Basic Features of the new design

A positive working, two-layer system was chosen and work began on designing a fully working plate (Table 1).

Clearly, one layer must be a printing image on press, which is highly resistant to solvents. If this layer is not to contain a switching mechanism then it must also be developer soluble. It follows then that this cannot be the top-layer in the assembly.

The top layer must then necessarily be developer insoluble in order to prevent removal of the solvent resistant base layer.

Next there must be a mechanism to allow imagewise switching of the developer insolubility.

Table 1: Plate functions by layer

Layer	Key Functions	
	New design	Physical insolubilization
Top	• Developer resistance • Solubility Switch	N/a
Base	• Solvent resistant printing image • Absorber	• Developer resistance • Solubility Switch • Printing image • Absorber

Imaging mechanism

There are a number of different options that would be available for imaging mechanisms for the top-layer.
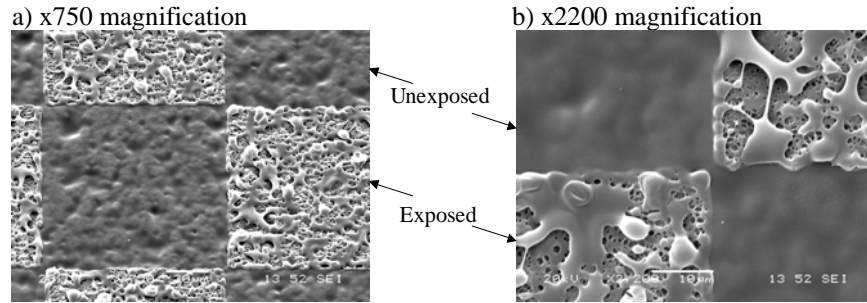
Physical insolubilization – This inhibition mechanism, described previously, is an option. However, such a plate assembly would still require conditioning in order to provide a stable imaging speed on keeping. Within KPG, the decision was made not to pursue a route that required both the conditioning process in addition to multiple layer coating.

Ablation – Many systems are described in the literature for ablative layers that would allow imagewise removal of an insoluble top-layer. However, these systems require a debris collection system in the platesetter to prevent build up of debris on optics. KPG decided that such an additional capital cost for the customer was to be avoided.

Physical deformation – The route chosen by KPG was to use a layer that would undergo a non-ablative, physical deformation, imagewise providing holes in the layer, allowing penetration of the developer through to the base layer.

Figure 3 shows SEM images of the exposed and unexposed areas of Kodak Polychrome Graphics SWORD Excel, where it can be seen that the exposure of the plate has caused a melting, and subsequent deformation of the top layer. This demonstrates the solubility switch involved in this mechanism.

Figure 3: SEM image of 50% dot area of SWORD Excel prior to development

a) x750 magnification

b) x2200 magnification

Unexposed

Exposed

Developer choice

One advantage over a physical insolubilization top-layer is the potential to choose a variety of developers for the plate system. Due to the requirement for H-bonding resins in the insolubilization process, such plates necessarily require the use of high pH developers, typical of conventional positive plate designs (Table 2). This new physical deformation system, however, does not necessarily require break-up of the top-layer during the development process for image discrimination. The minimum requirement is that, after developer has penetrated, the top-layer is lifted off the plate with the base coat in the imaged areas.

Table 2: Typical developer compositions

A Typical, low pH, Solvent Based Developer	A Typical High pH Developer
60 to 80 wt% water	50 to 70 wt% water
0.5 to 15 wt% of solvent, e.g. phenol ethoxylates, phenol propoxylates, benzyl alcohol, 2-ethoxyethanol, 2-butoxyethanol.	>20 wt% alkali metal silicate and/or hydroxide
3 to 8 wt% of an anionic, nonionic or amphoteric surfactant	0.01 to 10 wt% by weight of an image protecting surfactant
1 to 5 wt% pH buffer, e.g. ethanolamine, diethanolamine or triethanolamine	<0.1% colorant dye
<1 wt% antimicrobial and/or antifungal agents	
pH = <10.5	pH = >12

The first commercial version of this product was tailored to work with a lower pH, solvent-based developer (Table 2), in fact one of KPG's conventional negative plate developers. A second version of this plate type demonstrated at drupa 2004 has been tailored for use with high pH developers as used with other NPH plates. Resin design variations are required to allow this tailoring of properties, these will be described later, and so choice of the system developer is a key first step before designing the plate components.

Base layer design

The minimum plate functional requirements for the base layer resin are solvent resistance and developer solubility. However, manufacturability of the resin is also important and will be described. This was the first major challenge for the plate designers.

Before describing the specific resins, a short comment about the solvents that are a concern for the plate designer is useful. Typical alcohol substitute fountain solutions now use butyl cellosolve (BC, 2-butoxyethanol) and this is the solvent that can attack uncrosslinked novolak films. The lab testing for this property is often carried out by visual coating loss, or gravitmetric coating loss, of a dry film after varying times exposed to BC/Water mixtures. The water is key to help replicate the press conditions as this often times will swell a coating and allow penetration by the solvent. In UV print applications the plate wash solution is the aggressor, and the specific solvent is typically diacetone alcohol (DAA, 4-hydroxy-4-methyl-2-pentanone). Lab testing with aqueous mixtures is again used.

The copolymer design that was chosen as the basis for the KPG base layer comprised the monomers shown in figure 4.

Figure 4: KPG solvent resistant copolymer design

10 – 30 mol%   30 – 55 mol%   20 – 40 mol%
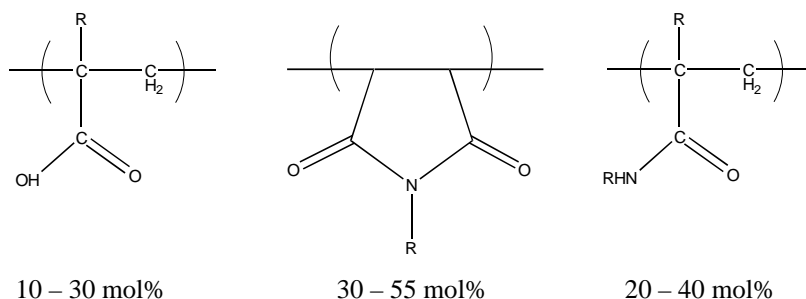
The film weight of this base layer is preferred to be between 0.5 and 2.5 g/m^2. Each monomer plays an important part in the resin properties:

Developer solubility: The (meth)acrylic acid provides the developer solubility for the base layer. The levels may vary depending on the pH of the chosen developer. In order to work in lower pH developers, the percentage is at the higher level of the range described.

Table 3 shows the effect of reducing acid level on developer solubility in Kodak Polychrome Graphics 956 Developer

Table 3: Time for 956 developer to penetrate film (84.5 % copolymer, 15% IR dye, 0.5% coating surfactant)

	Copolymer Composition			956 Developer Drop Test / seconds
	N-phenyl maleimide	Methacrylamide	Methacrylic Acid	
Polymer A	40	30	**30**	**2**
Polymer B	38	34	**28**	**4**
Polymer C	41.5	37.5	**21**	**8**

Solvent resistance: The N-substituted maleimide provides the solvent resistance for the baselayer. Lower levels can be sufficient to provide robust resistance to BC, and hence alcohol substitute founts, but in order to achieve good DAA resistance, higher levels, greater than 40% are required. R in these monomers is often chosen as a simple aromatic, as such materials are commercially available, such as N-phenyl maleimide (PMI).

Table 4 shows the effect of increasing N-phenyl maleimide level on the resistance to a common solvent in UV ink washes.

Table 4: Time for diacetone alcohol/water (80 :20, v:v) to penetrate film (84.5 % copolymer, 15% IR dye, 0.5% coating surfactant)

|	Copolymer Composition			DAA/Water Drop Test / minutes
	N-phenyl maleimide	Methacrylamide	Methacrylic Acid	
Polymer D	**38**	32	30	**3**
Polymer E	**45**	35	20	**5**
Polymer F	**50**	35	15	**8**

Ease of synthesis: The (meth)acrylamide can provide some level of solvent resistance, and also helps with even dissolution of the base layer in the

developer, rather than skinning, or removal in chunks. However, a far more pragmatic role of this hydrophilic monomer is to facilitate ease of synthesis. The target is to prepare copolymers that are resistant to solvents. This means they are difficult to dissolve in solvents, and so a delicate balance is required to prevent the polymers from gelling in the reaction vessel!

Many monomers are available to the polymer designer and a number of alternates have been successfully utilized. Other plate features can be introduced through additional monomer inclusion, such as bakability, if required. Alternately blends of different solvent resistant resins can be used to tailor properties.

In order to break some of the constraints of balancing the various requirements for the copolymer, monomers that can provide multiple functions, have also been studied. For example, the monomer in figure 5 helps ease of synthesis and provides bakability.

Figure 5: Bakable monomer
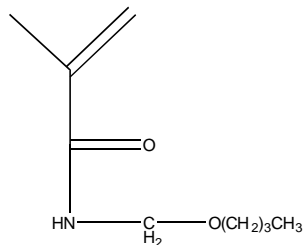
Bakable layers can be achieved with materials as described above, and can be enhanced by addition to the layer of crosslinker materials such as resoles (Table 5). Optimization remains crucial since too much resole can reduce the efficacy of the solvent resistant polymer. Shelf life of the base layer is good for the parent polymers described, however, this needs consideration when introducing reactivity into the base layer.

Table 5: Time for positive image deletion pen to remove film after baking at 230°C, for 8 minutes (84.5% polymer binder mixture, 15% IR dye, 0.5% coating surfactant)

	Polymer Binder Mixture			Time for complete removal of film / minutes
	Polymer C	Resole	Urea/acrylic copolymer	
Option 1	84.5	-	-	**<2**
Option 2	59.5	**10**	**15**	**>8**

Future designs will look to incorporate additional features, such as bakability, while maintaining the excellent properties of the resins currently commercially exploited.

Top layer design

The top layer has a number of performance criteria to meet, it must:

- o Resist developer in unexposed areas
- o Have good physical properties to prevent scratching
- o Be capable of physical deformation on heating, via laser exposure
- o Remove exposed areas from plate in the developer without "skinning"

This then led to the second major challenge in the design of this new plate as a number of variables are interconnected and the right balance is required.

Physical deformation on heating has not been a difficult feature to achieve, and as most resins, under the high temperature and short time exposure in the Thermal platesetters, will show this apparent melting, selection has not been constrained.

It is also relatively straightforward to select a resin that has a high resistance to the chosen developer. However, if the resistance is too high, and the material does not disperse well during processing then "overhang" will occur. "Overhang" was the biggest intuitive stumbling block to this plate mechanism. How do you prevent undercutting of the soluble base layer during the development process (figure 6)?

Figure 6: Schematic showing formation of overhang
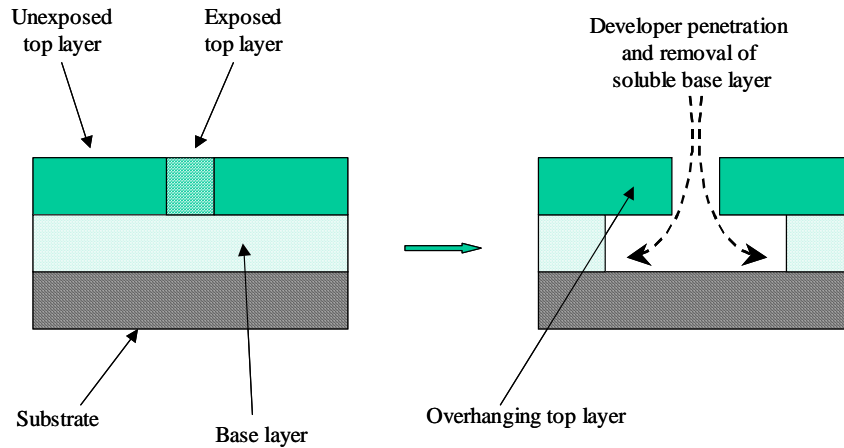
Early lab models used to prove feasibility utilized methacrylic acid polymers. These gave good developer resistance, across a wide range of developers, but came off in chunks in the developer. This led to poor resolution due to the overhang at the edge of dots (figure 7) and also necessitated aggressive brushing in the processor sections, to prevent topcoat chunks redepositing on the substrate.

Figure 7: Optical micrograph showing overhang at the edge of dots and redeposit in background
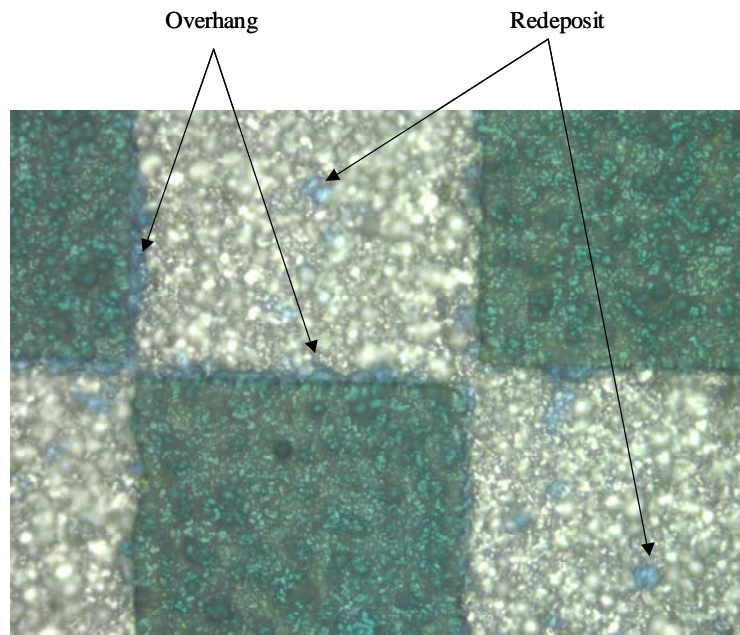
The problem was solved by careful choice of top layer resin to have some solubility in the developer to allow removal in a finer dispersion, balanced with optimization of the base layer solubility at the same time (figure 8). But the balancing act did not stop there.

Figure 8: Optical micrograph showing cleanly developed, sharp edges and clean background
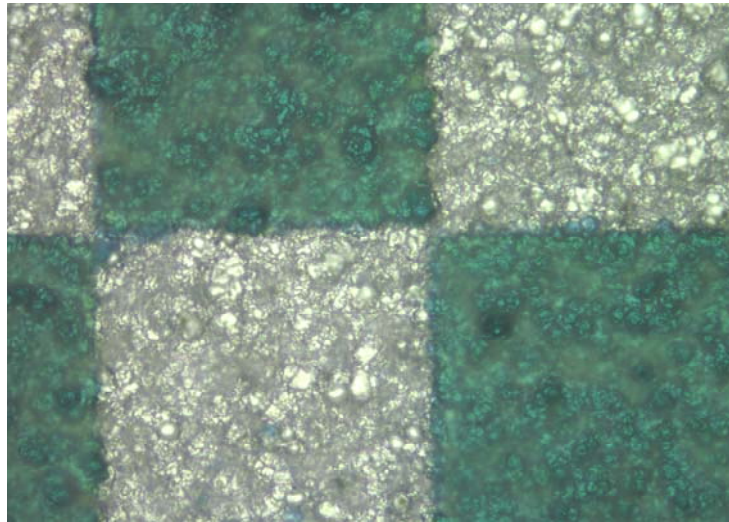
If the developer resistance of the top layer is too low, then a high film weight is required to provide developer resistance in the non-image areas. This will have a negative effect on imaging speed, as more energy is required to deform the thicker layer. Conversely, if the developer resistance is too high, then lower film weight will be required to allow development in exposed areas. This can give rise to problems of handling scratches, as any removal or partial damage of the top layer will expose the soluble base layer and lead to voids after processing. Top layer film weights are preferred between 0.5 and 1.0 g/m^2.

For both the low and the high pH developer systems, phenolic resin compositions have proved useful. Development rate can be fine-tuned by the control of the novolak type used or the use of substituted novolaks, i.e. esterification of a proportion of the phenolic groups to, for example, a simple tosylate. Many such materials with varying solubilities are conveniently available for consideration.

For the low pH developer version, SWORD Excel, the main resin is a simple m/p-cresol novolak and the resistance has been fine tuned through addition of a more resistant substituted novolak. This top layer resin is not truly soluble in the developer and a small level of filtration is required in the processor.

For the high pH developer version, Kodak Polychrome Graphics SWORD Ultra, more inhibition is required to provide developer resistance. In this case the single resin utilized is a tosyl esterified novolak, with esterification levels tailored to the required resistance point. In this case, though developer resistance in the dried film is high, once circulating in developer the resin will truly dissolve (the deprotonation of sufficient phenols to solubilize the resins chains is slow enough to provide developer resistance, but quick enough that it will usefully dissolve in the developer tank in a reasonable timescale).

The direction of current design efforts is to remove any requirements for filtration with low pH developers and to improve robustness to allow designs for any existing processor configuration in the field today.

IR absorber

As this is a pure heat effect, rather than a sensitization, it has been found that the position of the IR absorber in such a system is not critical. The heating can be achieved with the absorber in the top-layer itself, but also it can be achieved by absorption in an under-layer and conduction into the top-layer. The system can function with the absorber as a third, separate layer between the top-layer and developer soluble base layer, or through incorporation in the base layer itself. In addition, dyes and pigments can be used in the assemblies.

The commercial plates derived from this technology use the IR absorber in the base layer, typically comprising 5 – 20% of the base layer film weight. This design was chosen primarily to prevent any ablation events associated with over exposure. However, there are disadvantages of the other routes: as phenolics comprise the top layers, use of IR dye, which are typically also inhibitors, would lead to potential shelf life issues unless the top layer was conditioned; coating a separate layer of absorber, though potentially cost efficient due to lower levels required, this does add unwelcome complexity to the manufacturing process.

Solvent constraints in manufacturing

The final hurdle relates to the manufacturing of this plate assembly. It is found that any mixing of the base and top layers in the assembly degrades the performance of the plate, particularly imaging speed. Solvents for the topcoat and the topcoat drying parameters have to be carefully chosen in order to ensure that the layers remain discrete.

Conclusion

A new generation, NPH plate that has excellent unbaked solvent resistance has been described. The new plate is a two layer assembly that has allowed a separation of the various functions required in such a plate to separate material properties in to separate layers. The solvent resistant of this plate is excellent and provides good runlength, without the need for post-baking, in alcohol substitute fount press conditions, and in UV printing applications. The constraints of the physical insolubilization system are described and the new system demonstrates how to evade these problems.

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