Journal of Imaging Science and Technology® 53(2): 020504–020504-4, 2009.

Molecular Mechanism of the Water Vapor Treatment of Thermal Printing Plates

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Abstract. *Thermal printing plates based on novolak, a phenol-formaldehyde condensation polymer, are now used by some 80% of the printing industry worldwide. Until recently, the image discrimination of these plates; i.e., the difference in the dissolution rate between exposed and unexposed areas was only moderate. About three years ago it was discovered that treatment of the plates with water vapor substantially improves image discrimination. This treatment is now an important manufacturing step, but there is no generally accepted explanation of the water vapor phenomenon. We venture to offer such an explanation and are exploring its consequences for the performance of the thermal plates. © 2009 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.2009.53.2.020504]

INTRODUCTION

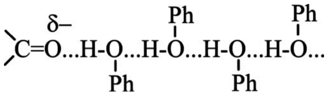
Thermal printing plates based on novolak, a phenol-formaldehyde condensation polymer, are now the most popular medium of the printing industry. The plates are ideally suited for the "Computer-to Plate" methodology and besides that they do not require a darkroom. The plates have two problems: compared with polymer plates or silver halide plates their radiation sensitivity is low, and that excludes them from use in some daily newspapers. Originally their image discrimination was not high; i.e., the difference in the dissolution rate of exposed and of unexposed parts of the plate was only moderate. Recently, a procedure was discovered that addresses this aspect of thermal plates. It consists of a prolonged treatment of the plates with water vapor at somewhat elevated temperature. Typically, the plates are subjected for 2 to 3 days to a water vapor atmosphere of 50% relative humidity (RH) while being kept at about 60°C. This treatment substantially improves image discrimination.[1]

The water vapor treatment is applied at the site of the plate manufacturer and its results, remarkably, persist for a very long time. Thus, they survive shipment to the end user and storage at the printing facility. The treatment is well known in the community of plate manufacturers, but no mention of it appears in the technical literature. That is because the improvement in plate performance is not thought to be caused by a specific effect, but is seen to be the result of a general settling down of the plate surface. Consequently, the treatment is variously called "plate stabilization," "plate maturation," or "artificial aging."

Although the water vapor treatment is now routinely applied by all large plate manufacturers and has in fact become an important step in the manufacturing process, there does not seem to exist a generally accepted explanation for why the water treatment works as it does. Here we venture to offer such an explanation, a potential "theory" of the water vapor effect in thermal printing plates.

FUNCTIONAL MECHANISM OF THERMAL PRINTING PLATES

The working mechanism of thermal plates is based on the formation of hydrogen-bonded connections among the OH groups of the novolak resin. These hydrogen bonds are formed by the interactions of the phenolic OH groups with each other and the succession of those hydrogen bonds produces in the resin a network of interconnected phenolic strings.[2,3] In the strings the protons of the OH groups are bound simultaneously to two oxygen atoms, to one by a single covalent H–O bond, to the other by a hydrogen bond, H…O. When molecules with highly polar groups or negatively charged ions are added to the system the hydrogen bonds in the strings are made stronger, the protons are more tightly bound, lowering thereby the acidity of the polymer. Since the dissolution rate of the resin in alkali depends on its pKa, the dissolution of the resin is inhibited in the presence of negatively charged sites. As a result highly polar groups (sulfones, ketones) or negatively charged ions act as dissolution inhibitors in novolak resins.



$$>C=\overset{\delta-}{O}\ldots H\text{-}\underset{Ph}{O}\ldots H\text{-}\overset{Ph}{O}\ldots H\text{-}\underset{Ph}{O}\ldots H\text{-}\overset{Ph}{O}\ldots$$

Exposure of the plates to an infrared laser disrupts the phenolic strings and removes the inhibition. In the exposed areas the plate is de-inhibited and becomes soluble in the alkaline developer. That is the basis of image formation in thermal plates.[3]

PROPOSED MECHANISM OF THE WATER VAPOR EFFECT

The interpretation of the mechanism of the water vapor effect is predicated on an observation we made on a group of aromatic ketones. When we used these ketones, flavanone,

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Received Oct. 11, 2008; accepted for publication Dec. 23, 2008; published online Mar. 10, 2009.
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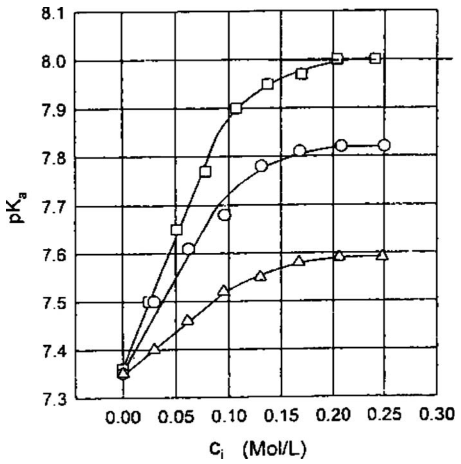
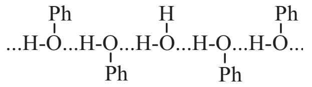


Figure 1. pKa of a novolak resin in the presence of flavanone, flavone, and naphthoflavone, as a function of inhibitor concentration in the resin. (Measured in a 1*M* solution in 95% acetonitrile/5% water; see Ref. 4).

flavone, and α-naphthoflavone as dissolution inhibitors of novolak, they differed strongly in their effect on the acidity (pKa) of the resin; yet, significantly, their effect saturated at the same molar ketone concentration.[4]

Saturation of the *p*H effect means that all the OH groups of the resin have been captured into phenolic strings. In the systems described in Figure 1, which refer to *p*H measurements in 1 mol/l phenol solutions, saturation of the *p*H effect occurs at inhibitor concentrations of 0.2 mol/l. That means that every inhibitor molecule is associated on average with five phenol groups. The string length is therefore five OH groups per string for any of the three inhibitors. Since the three ketones differ substantially in inhibition strength the length of the phenolic strings cannot be determined by the strength of the inducing inhibitors. We believe that, instead, it is determined by the statistics of the spatial configurations of the OH groups in the resin.

We propose the following mechanistic scenario. As the string grows from the inducing charged site, it eventually reaches an OH group that has no other OH group within reach and can therefore no longer form another hydrogen bond. It is our contention that at this point the water treatment intervenes. At the gap between the two aforementioned OH groups, a water molecule may intercalate itself and bridge the gap.



$$\ldots H\text{-}\overset{Ph}{O}\ldots H\text{-}\underset{Ph}{O}\ldots H\text{-}\overset{H}{O}\ldots H\text{-}\underset{Ph}{O}\ldots H\text{-}\overset{Ph}{O}\ldots$$

The water molecule can form hydrogen bonds with both OH groups and thereby increase the length of the phenolic string by another sequence of OH groups. As a result, the surface layer which alone contains the intervening water molecules is more strongly inhibited than the bulk of the film. It is this surface effect which increases image discrimination.

HYDROGEN BONDING BETWEEN PHENOLIC OH GROUPS

The formation of hydrogen-bonded strings in the novolak resin is based on the reciprocal interaction of phenolic OH groups. We can demonstrate this effect in the infrared absorption spectra of phenol dissolved in carbon tetrachloride. Figure 2 shows the relevant part of the spectrum at four different phenol concentrations. The sharp absorption peak at 3614 cm^{-1} belongs to the stretching vibration of the free OH bond. This assignment is supported by recent measurements on molecular beams of phenol,[5] where the sharp absorption line lies at 3657 cm^{-1}. The broad absorption centered at 3260 cm^{-1} belongs to the hydrogen-bonded OH groups and that assignment is supported by the absorption of liquid phenol in a Nujol mull,[6] which peaks at 3229 cm^{-1}. In light of these data it may be deduced that in the 0.08*M* solution the hydroxyl groups are (almost) completely free, but in the 1.0*M* solution the autoassociation of phenol is 88% complete.

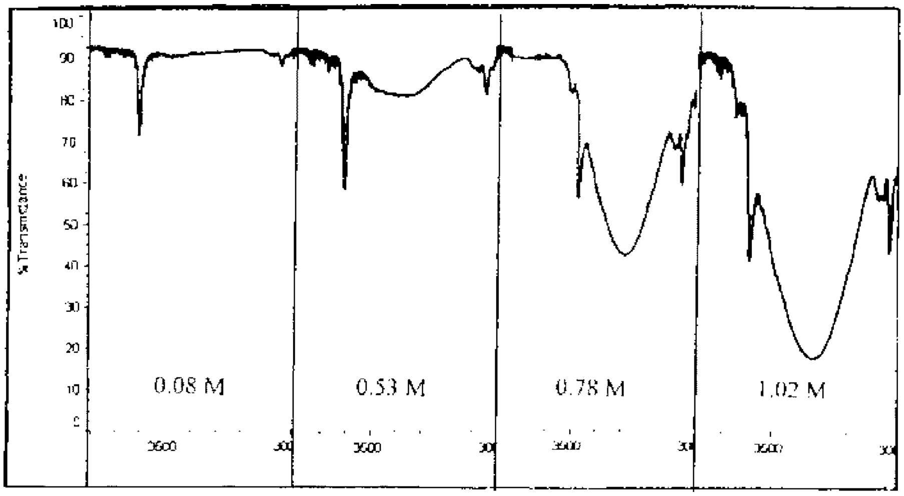


Figure 2. Part of the IR spectrum of phenol dissolved in CCl$_4$ at four different concentrations: 0.08*M*, 0.53*M*, 0.78*M*, and 1.02*M*.

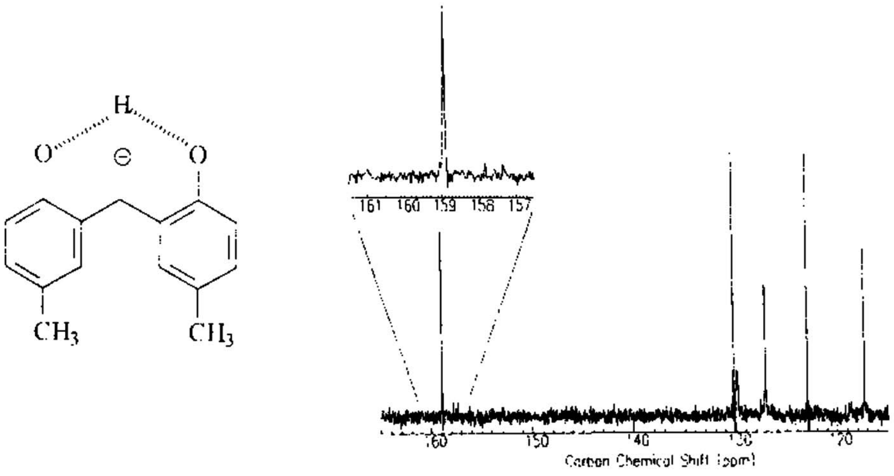
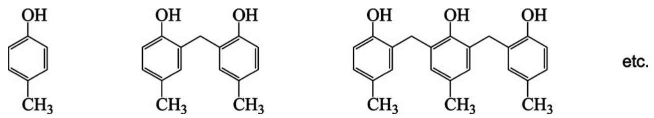
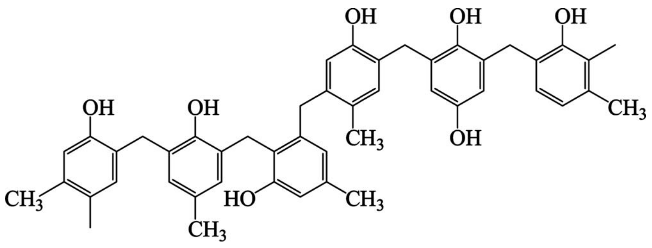


Figure 3. ^{13}C NMR spectrum of the tetraethylammonium salt of the *p*-cresol dimer (0.1 g in 1 mL) in a 1*M* solution of tetraethylammonium chloride in DMSO. Inset: enlarged trace of the C–O carbon signals.

To find out whether the OH groups of novolak are able to interact with each other in this way, we chose oligomers of para-cresol as a model system[7]



These oligomers can be looked upon as the building blocks of novolak.



We found that in the oligomers of para-cresol there is indeed strong interaction between vicinal phenol groups. For example, in the negative ion of the *p*-cresol dimer, the bonds of the proton to either of the oxygen atoms are indistinguishable from each other. In the ^{13}C NMR spectrum of the ion in dimethylsulfoxide (DMSO), the two CO groups on the aromatic rings produce a single line. (See Figure 3.) That means that the proton of the OH group has moved halfway to the second oxygen; an indication of intense hydrogen bonding.[7]

This behavior suggests that there is a similar interaction between the vicinal OH groups of novolak, and that there is in novolak films a preexisting network of hydrogen-bonded strings even in the absence of an inhibitor. The introduction of a dissolution inhibitor merely reinforces the hydrogen bonds, and that leads to a stronger immobilization of the protons within the strings. The result is a substantial lowering of the acidity of the resin, as is illustrated convincingly in Fig. 1. Since the dissociation of protons is the first step in the dissolution of novolak,[3] the presence of the inhibitors lowers the dissolution rate.

At the usual level of inhibitor concentration (5% approximately), only a limited number of OH groups is part of those phenolic strings that originate at the inhibitor. Most other OH groups in the resin are not part of these strings. The water molecules of the treatment intervene here and attach some of the so far unconnected sequences of OH groups to the phenolic strings emanating from the inhibitors. This increases the concentration of immobilized protons and lowers the dissolution rate. At the same time it increases the radiation dose required to disrupt all phenolic strings and reestablish the original dissolution rate of the resin. We have information indicating that exposure to a moist atmosphere (50% RH) at 30°C increases the radiation dose requirement of a plate from 80 to 100 mJ/cm^2; in films exposed to such an atmosphere at 45°C, the radiation requirement increases to 170 mJ/cm^2. These data[1] are a clear indication of increased surface inhibition, which is the essence of the water vapor effect.

THE LENGTH OF THE PHENOLIC STRINGS

The length of the phenolic strings is an important datum for the function of thermal plates as well as for the evaluation of the water vapor effect. There is no viable method to estimate the length of the strings in solid polymer films. The *p*H measurements in Fig. 1 were performed on solutions of novolak at a 1*M* concentration of phenol groups, which is equivalent to 9% weight of phenol in the solution. At that concentration, the novolak chains are effectively separated from each other. Saturation of the inhibitor effect was reached in these experiments at a 0.2*M* inhibitor concentration corresponding to an average string length five OH groups per string. Because the polymer chains in these solutions are separated from each other, in these experiments the phenolic strings were all formed within single polymer chains and they are shorter than the strings that will develop in a solid novolak film.

That the string length in solid polymer films is distinctly larger than in dilute solution is supported by glass transition measurements[8] on solid novolak films containing increasing

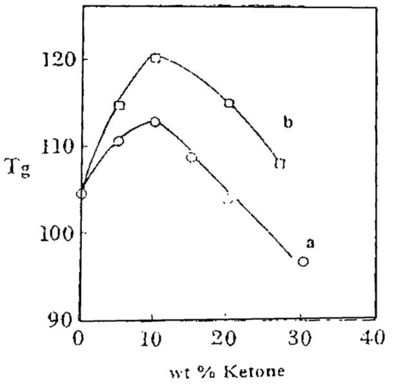


Figure 4. Glass transition temperature of novolak films containing the inhibitors: (a) flavone and (b) α-naphthoflavone.

concentrations of dissolution inhibitors. These are shown in Figure 4. While we are not able to give a quantitative estimate of the length of phenolic strings in these systems, we need to emphasize that all hydrogen bonds that contribute to an increase in the glass transition temperature are strictly intermolecular connections and that all of them originate at OH groups that are contained in the strings emanating from the dissolution inhibitors.

FURTHER SUPPORT FOR THE PROPOSED MECHANISM

The present model is based on the notion that water molecules allow the inductive effect of the originating dipole of the inhibitor to propagate further through the phenolic resin than it would in the absence of the water effect. This idea is supported by the following observations. If the plates are heated above 100°C, all water eventually evaporates from the plates and there is no surface inhibition at all. If such plates are then exposed to a pattern and not developed soon after exposure, the (latent) images, which have formed on them fade with time in the ambient atmosphere. They fade more slowly in a refrigerator, and they do not fade at all in a desiccator.[1] The latent image is defined in terms of disrupted phenolic strings. If it fades that means that the disruptions are "healed" by the arrival of connecting water molecules. This process cannot occur in the absence of water (in a dessicator) and it slows down at lower temperature. This shows that the repair of the disrupted phenolic strings in the exposed areas is in general accomplished by water molecules arriving from the atmosphere. The images fade even in a desiccator if the plates are kept at higher temperatures (in our experiments, above 80°C). At those temperatures, fading is caused by the rearrangement of parts of the polymer chain reconstituting some of the phenolic strings when the glass transition temperature of the polymer is $T_G = 105°\mathrm{C}$.

WHY THE WATER EFFECT CANNOT BE PRODUCED WITH LIQUID WATER

In plate production, the water vapor treatment presents a logistic problem and one may wonder why water is not supplied to the plates in liquid form. It turns out that this is completely ineffective. The surface of the polymer films on the plates is intensely hydrophobic and actively rejects the presence of water. If a drop of water is placed onto the film surface, the drop does not spread but remains on the surface unchanged, until it evaporates. Figure 5 shows a drop of water on the surface of the printing plate. The phenomenon is caused by the high surface tension of liquid water on the hydrophobic surface. Because of it, water molecules cannot enter the novolak film from the liquid phase; only water molecules from the gas phase can penetrate the film surface and occasionally find there a site where two OH groups are positioned in such a way as to anchor a water molecule between them. The probability of this happening is low and that is why the water vapor treatment takes a relatively long time (2 to 3 days).

Figure 5. Shape of a water drop on the surface of a dry printing plate.

It may be of interest to note that this behavior is not completely sui generis. A similar phenomenon is observed in the well known Gor-Tex® textiles[9] that are used in the manufacture of raincoats. These textiles are hydrophobic and repel water droplets, but allow water vapor to penetrate the material, making the garments much more wearable.

ACKNOWLEDGMENTS

The authors acknowledge substantive conversations with Jonathan Bentley of IPAGSA S.L., Rubi, Spain. We thank Sanja Natali of the Department of Chemical Engineering for the photograph of the water drop and for help with the presentation of this paper.

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