Percolation View of Novolak Dissolution. 6. The Acceleration of Novolak Dissolution by Phenolic Additives

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ABSTRACT: Phenols or polyphenols of low molecular weight are added to Novolak resists to increase the dissolution rate. They function as dissolution promoters by introducing additional hydrophilic percolation sites (OH groups) into the system. All low molecular weight phenols accelerate dissolution, but some are also able to improve lithographic performance by increasing the image contrast of the material, i.e., the difference in dissolution rate between exposed and unexposed areas of the resist film. Additives that function in this way are those that are included in the phenolic clusters formed by the inhibitor. It appears that the criterion for inclusion in the clusters is the acidity of the OH groups of the additive.

Introduction

In recent years there has been substantial progress in the lithographic performance of Novolak−diazoquinone resists. To a significant degree, these advances are based on the ideas of Hanabata and his colleagues,[1] who proposed the use of fractionated Novolak resins. While the high molecular weight fractions of Novolak are beneficial to lithographic performance, these resins have unacceptably slow dissolution rates. Hanabata overcame this difficulty by using diazoquinone inhibitors with free OH groups that acted as built-in dissolution promoters.[2,3] Since then, others have separated the functions of dissolution inhibition and dissolution promotion,[4] and dissolution promoters or accelerators have become important components of practical resist systems. This paper investigates the molecular mechanism of the dissolution promotion effect.

Accelerators as Additional Percolation Sites

Dissolution promoters are almost invariably low molecular weight phenol derivatives. It is our contention that they function by providing additional hydrophilic sites to the percolation field of the material. The dissolution of Novolak is a percolation process where a diffusant, the developer base, migrates in the solid resin film by transferring from one hydrophilic percolation site to the next.[5] The state of the percolation field is characterized by the percolation parameter, p, which is a measure of the density of percolation sites.[6] The dissolution rate, R, is linked to the percolation parameter by the so-called scaling law of percolative dissolution.

$$\log \frac{R}{R_o} = 2 \log \frac{p - p_c}{1 - p_c} = f(p) \qquad (1)$$

Here R_o is the dissolution rate of a reference resin (e.g., poly(vinylphenol) with $R_o = 77.1\ \mu$m/s), and the percolation threshold has the value $p_c = 0.20$. Figure 1 is a schematic representation of the scaling law.

In Novolak resins, the percolation sites are the OH groups of the phenol units. The arrival of an additional OH group increases the value of the percolation parameter and moves the image point of the system upward on the scaling law curve, thereby increasing the dissolution rate. We illustrate this idea by data obtained with 4-hydroxybenzophenone in a commercial Novolak resin. We prepared a series of films with increasing concentration of this accelerator and measured their dissolution rate in 0.2 N KOH. The experimental points are overlaid in Figure 2 on the scaling law function. The dissolution rate of the basic Novolak resin used for the experiment is $R(0) = 19.36\ \mu$m/min, and the position of the image point of the unaccelerated resin on the scaling law curve is $p(0) = 0.600$. We assume that the percola-

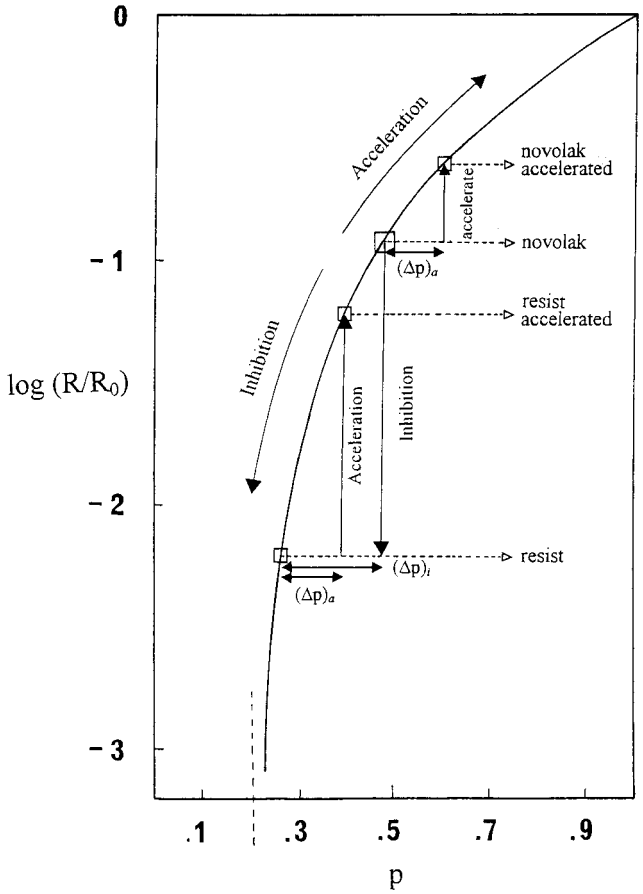

Figure 1. Dimensionless scaling law curve (eq 1). R is the dissolution rate, R_o is the dissolution rate of a reference resin, and p is the percolation parameter of the material, which is proportional to the concentration of hydrophilic percolation sites (OH groups).[7]

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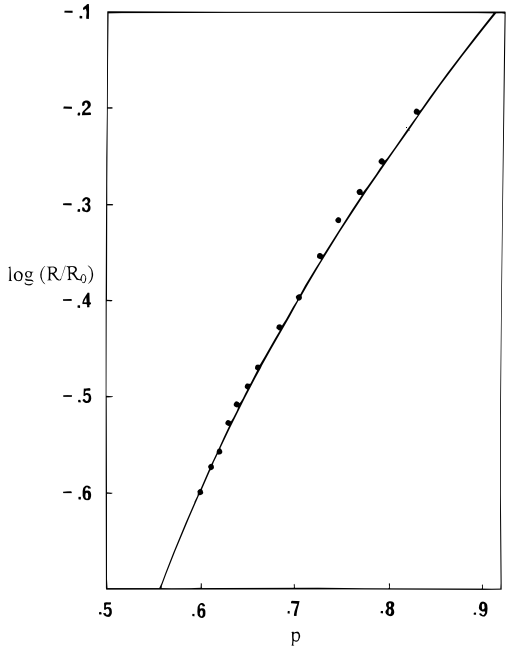

Figure 2. Comparison of the acceleration effect of 4-hydroxybenzophenone with the predictions of the percolative scaling law. log R/R_o is plotted as a function of $p = p(0) + \alpha c_a$, where p_o is the percolation parameter of pure Novolak ($p_c = 0.600$) and $\alpha = 1.29$. The factor α measures the effect of unit concentration of accelerator on the dissolution rate.

tion parameter of the accelerated film is a linear function of accelerator content.

$$p = p(0) + \alpha c_a \tag{2}$$

where α is determined from experiment. Figure 2 shows that the relation between dissolution rate and accelerator concentration follows the predictions of percolation theory rather accurately. We conclude that in pure Novolak the effect of accelerators is exactly that predicted by percolation theory for an additive that imports additional percolation sites into the system.

Another test for the accuracy of this interpretation is based on a relation between the derivative d log R/dc_a and the slope of the scaling law curve, d log R/dp (see ref 7).

$$f_{ac} = \frac{\mathrm{d} \log R}{\mathrm{d}c_a} = \mathrm{const}\, \frac{\mathrm{d} \log R}{\mathrm{d}p} = \frac{\mathrm{const}}{\sqrt{R}} \tag{3}$$

Here f_{ac} is the acceleration factor of the additive, and that is expected to be proportional to the slope of the scaling law curve *at the image point of the (unaccelerated) resin*. (This was shown in ref 9 to be proportional to the reciprocal square root of the dissolution rate, as indicated in the last term of eq 3.)

We have tested eq 3 by incorporating two different accelerators into a group of five partially methylated Novolak resins. These resins differ in their dissolution rates and have, consequently, different image points on the scaling law curve. It can be seen in Figure 3 that a plot of the acceleration factor vs the reciprocal square root of the dissolution rate of the resin (before acceleration) is linear. We conclude again that in pure Novolak films, accelerators simply change the number (density) of percolation sites.

All the phenolic derivatives we investigated acted as dissolution promoters. In Table 1 we give the accelera-

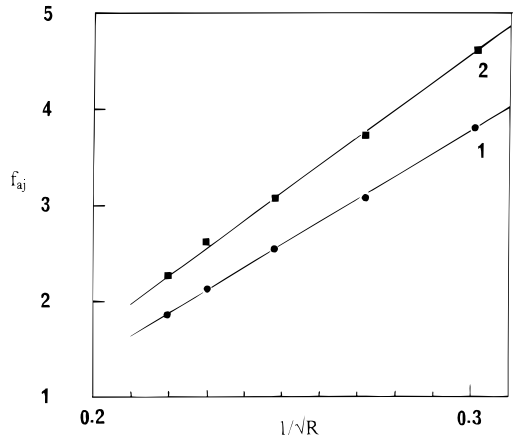

Figure 3. Test of eq 2. Plotting f_{ac} of two accelerators in several Novolak resins of different densities of percolation sites (OH groups), as a function of the slope to the scaling law curve. This slope is here represented by $1/\sqrt{R}$. Upper trace: 2,2′,4,4′-tetrahydroxybenzophenone. Lower trace: 4-hydroxybenzophenone.

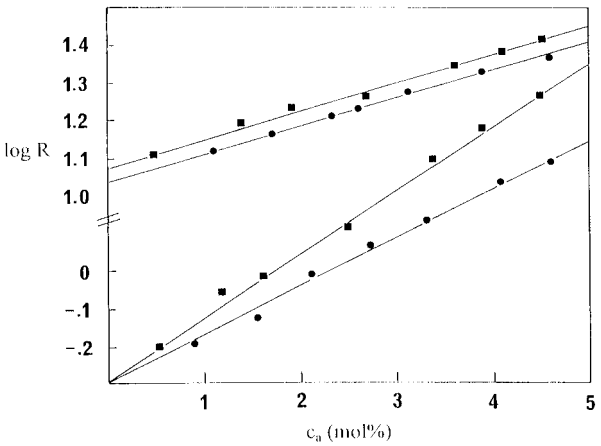

Figure 4. Inhibition effect of 4-hydroxybenzophenone (4-HBP, ■) and of 3-hydroxybenzophenone (3-HBP, ●) on the dissolution rate of an unexposed Novolak resist containing 8.2% DNQ (lower traces) and on the fully exposed resist (upper traces).

Table 1. Acceleration Effect of Hydroxyl-Substituted Benzophenones

position of OH groups	M	d log R/dc_a
2-	198	3.7
3-	198	4.4
4-	198	6.0
2,2′-	214	4.2
2,4-	214	5.7
4,4′-	214	6.8
2,3,4-	230	7.9
2,4,4′-	230	5.2
2,2′,4,4′-	246	7.9

tion factors, f_{ac} = d log R/dc_a, for a group of hydroxyl-substituted benzophenones in a typical Novolak resin.

Dissolution Accelerators and Photographic Contrast

The behavior of dissolution promoters in complete resists, i.e., in the presence of dissolution inhibitors, is more complex. The principal aspect here is that most accelerators increase the dissolution rate of unexposed resists more than that of exposed resists. We illustrate this in Figure 4 on 3-hydroxybenzophenone and 4-hydroxybenzophenone. While these results are in complete accord with the scaling law of percolation theory

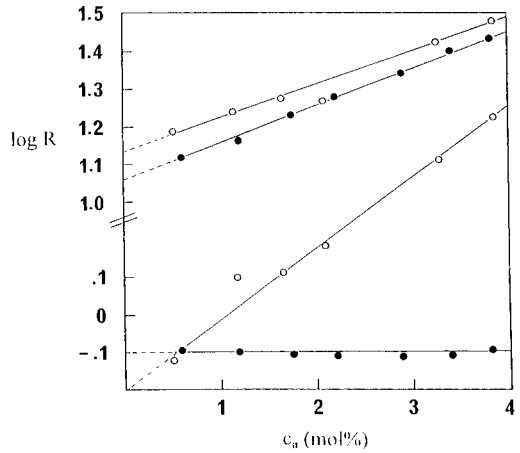

Figure 5. Inhibition effect of 2,4,4′-trihydroxybenzophenone (2,4,4′-THB, ○) and of 2,3,4-trihydroxybenzophenone (2,3,4-THB, ●) on the dissolution rate of Novolak resists containing 8.2% DNQ: unexposed resist films (lower traces) and fully exposed resist films (upper traces).

(see Figure 1), they have negative implications for the lithographic performance of accelerated materials.

Lithographic performance is determined by image contrast, and in Novolak resists that is based on the dissolution rate difference between exposed and unexposed areas of the resist films. The behavior shown in Figure 4 is clearly detrimental to image contrast. For an accelerator to improve contrast it has to *increase the dissolution rate of the exposed film more than that of the unexposed film*. Most accelerators so far considered behave similarly to 4-hydroxybenzophenone; however, among the hydroxyl-substituted benzophenones we found one that enhanced the lithographic contrast: 2,3,4-trihydroxybenzophenone (2,3,4-THB). This additive increases the dissolution rate of exposed resists but does not affect the dissolution of unexposed resists (see Figure 5).

The reasons for this behavior become clearer when we compare the acceleration effect of 2,3,4-THB in pure Novolak and in resins to which increasing quantities of inhibitor had been added. The results are shown in Figure 6. In the absence of inhibitor, 2,3,4-THB acts as a normal accelerator. However, when some 2% of the strong inhibitor α-naphthoflavone is added, the slope of the log R vs c_a plot becomes more shallow, and at 3% naphthoflavone, the plot is horizontal. If more inhibitor is added to the system, the zero slope of the plot is maintained to higher accelerator concentrations. We interpret this to mean that a given concentration of inhibitor can bind a certain quantity of accelerator within the phenolic clusters of the resist. At this point, we refer the reader to our description of the percolation-cum-phenolic-clusters model of Novolak resists.[8−10] The dissolution rate of a material is determined essentially by the concentration of percolation sites in the noncluster regions of the percolation field. As a result, phenols that are held within the clusters do not affect the dissolution rate. When the quantity of accelerator in the system exceeds that which can be held by the inhibitor, some of the phenols remain outside of the clusters and make their regular contribution to the dissolution rate.

Figure 6 refers to α-naphthoflavone as inhibitor, but similar behavior, somewhat less distinctly, is observed in the presence of diazonaphthoquinones. In Figure 7 we have plotted the limiting concentration, c'_a, that can be held by a given quantity of inhibitor as a function of

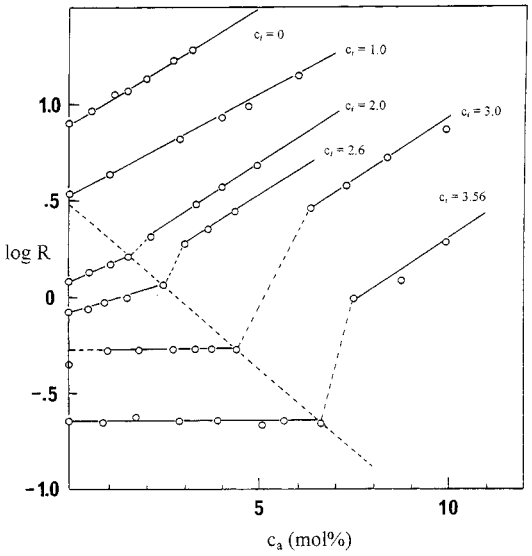

Figure 6. Effect of 2,3,4-trihydroxybenzophenone (2,3,4-THB) on the dissolution rate of pure Novolak and of resists containing increasing concentrations (c_i) of α-naphthoflavone: (top to bottom) 0, 1.0, 2.0, 2.6, 3.0, 3.56.

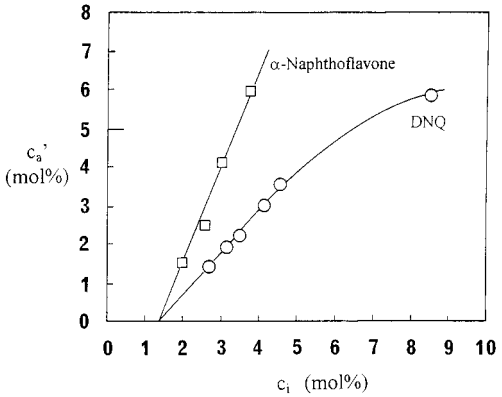

Figure 7. Effect of the inhibitor concentration, c_i, on the critical maximum concentration of accelerator, c'_a, that the inhibitor can hold within the phenolic clusters. The upper trace refers to α-naphthoflavone; the lower, to DNQ as inhibitor.

inhibitor concentration for α-naphthoflavone and for a typical DNQ, namely 1,2-naphthodiazoquinone-5-sulfonic acid 4-*tert*-butylphenol ester.

Inclusion of Accelerators in Phenolic Clusters

The beneficial effect of 2,3,4-THB on lithographic contrast is predicated on it being included in the phenolic clusters of the resist. What is the criterion for the inclusion of an additive in the clusters? In this context, we recall that clusters are formed in the coating solution where the inhibitor (hydrogen acceptor) is presented with an ensemble of phenols, polymer-bound and free, of varying hydrogen-donating ability. The inhibitor will preferentially interact with the strongest hydrogen donors first and that means that phenols with the lowest pK_a value are more likely than others to be included in the clusters. The criterion for inclusion of an additive is the acidity of its phenol group.

Why should 2,3,4-THB be more acidic than the isomeric 2,4,4′-THB? The relevant distinction is the vicinal position of its OH groups. This allows these to interact with each other, and the interaction loosens the protons of the hydroxyls and increases their acidity. We note that 2,3,4-trihydroxydiphenylmethane (Figure 9) shows a similar behavior, and the same is true of

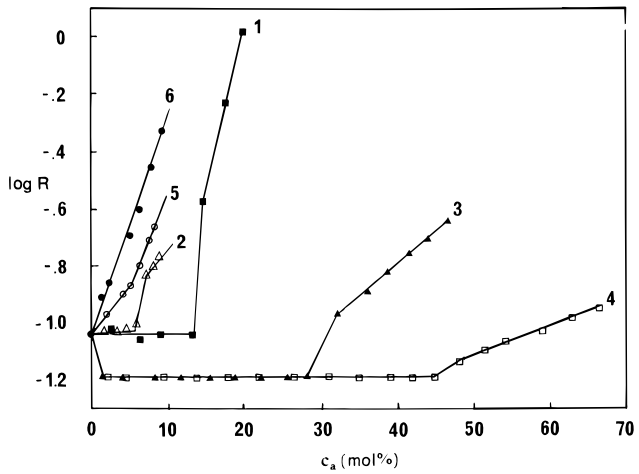

Figure 8. Effect of various accelerators on the dissolution rate of resists containing 6.2% of the inhibitor α-naphthoflavone: (1) 2,3,4-trihydroxybenzophenone; (2) 2,3,4-trihydroxyacetophenone; (3) 2-hydroxybenzophenone; (4) 2,2′-dihydroxybenzophenone; (5) 2,3-dihydroxynaphthalene; (6) 1,3-dihydroxynaphthalene.

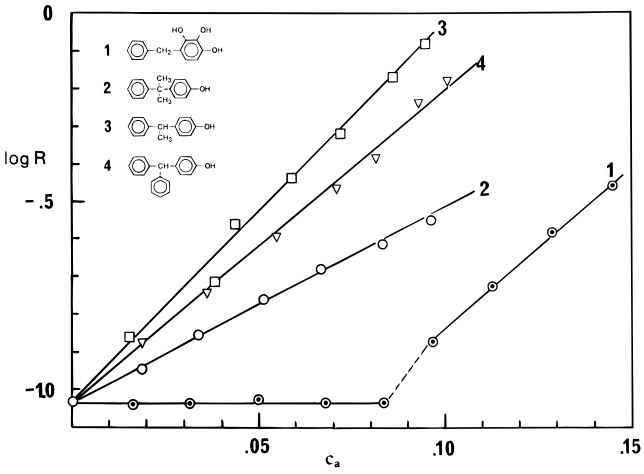

Figure 9. Effect of several hydroxyl-substituted diphenylmethanes on the dissolution rate of a Novolak resin containing 6.2% DNQ.

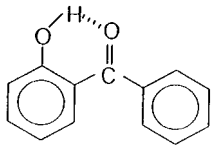

Figure 10. Phenol−carbonyl interaction in 2-hydroxybenzophenone.

2,3,4-trihydroxyacetophenone (Figure 8). Furthermore, 2,3-dihydroxynaphthalene (Figure 8) shows the tell-tale break in the log R vs c_a plot, and 1,3-dihydroxynaphthalene does not. However, it is not the vicinal position of the hydroxyls per se that is responsible for this behavior, but the resulting acidity. That is demonstrated by the behavior of 2-hydroxybenzophenone and of 2,2′-dihydroxybenzophenone, in Figure 8. Here the increase in acidity is caused by the interaction of the OH group in the 2-position of the aromatic nucleus with the nearby carbonyl group, forming a sterically advantageous six-membered ring with the hydrogen bond (Figure 10). The view that it is the acidity of the OH group that decides membership in the phenolic clusters is further supported by the behavior of α-naphthol and 4-chloro-α-naphthol, shown in Figure 11. Here the

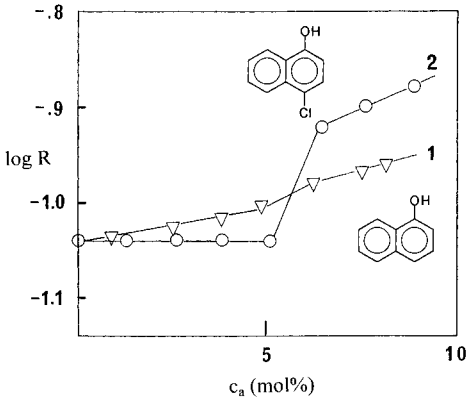

Figure 11. Effect of α-naphthol (1) and of 4-chloro-α-naphthol (2) on the dissolution rate of a Novolak resist containing 6.2% DNQ.

Table 2. Inhibition Effect of 4-Hydroxybenzophenone in the Presence of Increasing Concentrations (c_i) of DNQ

c_i (%)	d log R/dc_a	$\sqrt{R}$
0	4.5	0.30
5.5	5.4	0.71
8.64	6.7	1.10
10.5	7.8	1.52
11.1	9.7	1.96
11.8	11.0	2.20
12.5	11.45	2.91
12.8	12.0	3.5
13.1	12.7	4.26
13.7	13.5	4.75
14.2	14.6	5.35

increasedacidity is produced by an electron-withdrawing substituent in the 4-position of an aromatic ring.

Although these results are convincing, they are somewhat anecdotal. On the suggestion of one of the reviewers, we plan to undertake a more thorough study where we hope to correlate the limiting accelerator concentrations with the pK_a values of the additives.

Accelerators in the Presence of High Concentrations of Dissolution Inhibitors

The behavior of dissolution promoters in the presence of high concentrations of dissolution inhibitors is quite complex. We have explored it on the example of 4-hydroxybenzophenone in a conventional Novolak resin to which increasing quantities of a common monofunctional DNQ inhibitor have been added. The results are recorded in Table 2. The acceleration effect increases with increasing DNQ content, but not in a linear fashion. The significance of the data becomes clearer if we plot d log R/dc_a against $1/\sqrt{R}$ (see Figure 12). Here $1/\sqrt{R}$ represents the slope of the scaling law curve at the image point of the inhibited, but unaccelerated, resist. In pure Novolak films such plots are linear (see Figure 3), but in the presence of inhibitor they are clearly nonlinear and they consist of two branches.

This strange result can be qualitatively understood if we recall that the introduction of an inhibitor (DNQ) into Novolak leads to the formation of phenolic clusters. The clusters concentrate some of the hydrophilic sites near the inhibitors and leave the surrounding regions somewhat depleted of sites. The diffusivity of base is determined in essence *by the concentration of hydrophilic sites in the noncluster regions*.[8] As a result, the effect of a phenolic additive on the dissolution rate depends on whether or not the additive is included in the phenolic clusters. From the discussion in ref 9 it follows that not all OH groups have the same ability to

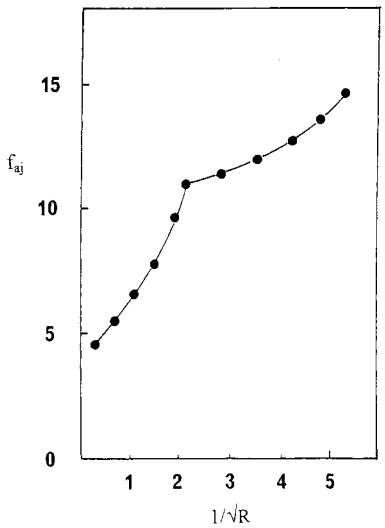

Figure 12. Effect of 4-hydroxybenzophenone on the dissolution rate of a Novolak resin in the presence of increasing concentrations of a standard DNQ inhibitor. The acceleration factor f_{aj} is here plotted vs the slope of the scaling law curve, represented by $1/\sqrt{R}$.

participate in clustering. The criterion here is the hydrogen-donating ability of the phenol, in other words, its acidity. In the casting solution of the film, the inhibitor (DNQ) will preferentially attract phenol groups with strong hydrogen donor properties. For that reason, at low inhibitor concentrations the phenolic clusters will at first contain mainly the superacidic phenols of Novolak, and the accelerators, which have the lower acidity of monomeric phenols, will be excluded from the clusters. Because of this, they will add to the site concentration outside the clusters and increase the dissolution rate. As the inhibitor content of the system is increased, more of the resin-bound phenols are taken into the clusters, the concentration of the original OH groups outside the clusters decreases, and the addition of a constant quantity of accelerator molecules (which at this stage still remain outside) will correspond to a larger fraction of the percolation sites outside the clusters and will make a progressively larger impact on the dissolution rate. That, we believe, is the reason for the supralinear shape of the plots in Figure 12.

As regards the discontinuity of the plot in Figure 12, we believe that it marks the point where the DNQs of the system have bound all the superacidic phenols available in the coating solution. Additional quantities of inhibitor now start to retain in the clusters also monomeric phenols of lower acidity, and that includes the accelerators. Accelerators that are now partly absorbed into the clusters do not any more contribute as much to the site concentration outside the clusters as before, and that is expressed in the lower slope of the second branch of the plot in Figure 12.

In summary: The behavior of conventional accelerators in unexposed resist films depends on whether or not they are included in the phenolic clusters of the inhibitor. At low inhibitor concentrations, most accelerators remain outside the clusters and do increase the concentration of active hydrophilic sites. Above a certain inhibitor concentration, accelerators start to be accepted into the clusters, and at that point their effect on the dissolution rate is reduced. In both regimes the effect of a constant quantity of accelerator depends on the phenol concentration outside the clusters, and as that concentration decreases, the effect of the accelerators increases.

Conclusions

Phenolic accelerators increase the overall concentration of hydrophilic percolation sites in Novolak films, and their effect on the dissolution rate is exactly that predicted by percolation theory for an additive that imports an additional dose of percolation sites into the system. In the presence of inhibitors, the effect of accelerators on the dissolution rate depends on whether the OH groups of the accelerator are included in or excluded from the phenolic clusters of the unexposed resist. Phenols that are included in the clusters make no, or only a small, contribution to the dissolution rate, while phenols that remain outside the clusters increase the dissolution rate considerably.

Whether or not an accelerator molecule is included in the phenolic clusters depends on its hydrogen-donating ability, i.e., on the acidity of its OH groups. The acidity increase brought about in polyphenolic accelerators by the hydrogen-bonding interaction between vicinal OH groups is often sufficient to bring the accelerators into the clusters. Alternatively, acidity increases can be achieved by substitution in the aromatic network. These results strongly support the validity of the percolation-cum-phenolic clusters approach to Novolak resists.

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