A Percolation View of Novolak Dissolution. 3. Dissolution Inhibition

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ABSTRACT: The dissolution of novolak films in aqueous alkali is controlled by the diffusion of base through a thin penetration zone that forms at the interface with the developer solution. Base diffusion is a percolation process in which ions of the base migrate through the zone by stepping from one hydrophilic site (phenol or phenolate) to the next. Dissolution inhibitors function by blocking some of the hydrophilic sites and thereby interrupting the diffusional pathways. Percolation theory suggests a relation between the strength of inhibition and the percolation characteristics of the resin. The two are linked by the hydrophobic displacement volume of the inhibitor. The hydrophobic displacement volume depends not only on the space requirements of the inhibitor but also on the mobility (or immobility) of the hydrophilic sites in the resin matrix; it is much smaller above the glass transition temperature of the penetration zone than below it, and it is smaller in systems where some degree of motional freedom persists even below the glass transition of the zone. The hydrophobic displacement volume is the fundamental figure of merit of an inhibiting additive in a given base resin.

Introduction

The addition of small quantities of a naphthodiazoquinone derivative to novolak dramatically lowers the dissolution rate of the resin in aqueous alkali. This observation has become the basis of a whole class of photoresists which are currently the most important imaging materials of the semiconductor device industry.[1] The key to an understanding of these systems is the realization that novolak, and other phenolic resins, are amphiphilic materials which contain hydrophobic as well a hydrophilic components. In fact, a novolak film may be regarded as a hydrophobic solid in which hydrophilic sites, the OH groups of the phenols, are embedded. The dissolution of novolak is linked to the deprotonation of some of its phenol groups to phenolate ions. The rate of formation of phenolate is controlled by the rate of supply of base to the reaction site, i.e., by the diffusion of base into the solid matrix.[2] Base is attracted to the hydrophilic sites of the material and repelled by its hydrophobic regions. As a result, it migrates into the amphiphilic solid by stepping from one hydrophilic site to the next.[3,4] This process, termed percolative diffusion, depends on the availability of an unbroken sequence of hydrophilic sites.[5] Inhibitors function by blocking some of these sites and thereby interrupting the diffusional pathways.

This paper describes a relation between the inhibition effect of an additive and the percolation parameter of the resin, and it identifies the link between the two variables as the hydrophobic displacement volume of the inhibitor.

The Inhibition Factor and the Scaling Law of Percolative Dissolution

Meyerhofer, one of the first to study dissolution inhibition quantitatively,[6] has shown that a plot of the logarithm of dissolution rate (R) against the inhibitor concentration (c_i) is linear over a reasonable concentration range. Figure 1 is an example. The slope of the Meyerhofer plot may be used as a concentration-independent measure of the strength of the inhibition effect. It has been termed the inhibition factor f_{ij} of inhibitor i in resin j.

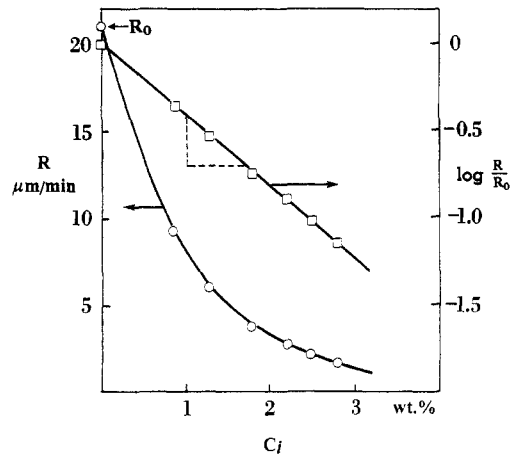

Figure 1. Dissolution rate as a function of inhibitor content (weight percent) in the solid resin film for the base resin of group III, inhibited with the standard monofunctional diazoquinone inhibitor used in this study.

$$f_{ij} = -\mathrm{d} \log R/\mathrm{d}c_i \quad (1)$$

Because the inhibition factor is defined in terms of log R, we have presented the scaling law of percolative dissolution[4] by plotting in Figure 2 log R as a function of the percolation parameter p.

$$\log R = \text{const.} + 2 \log(p - p_c) = f(p) \quad (2)$$

The percolation parameter p is related to the density of percolation sites, which in novolak are the OH groups of

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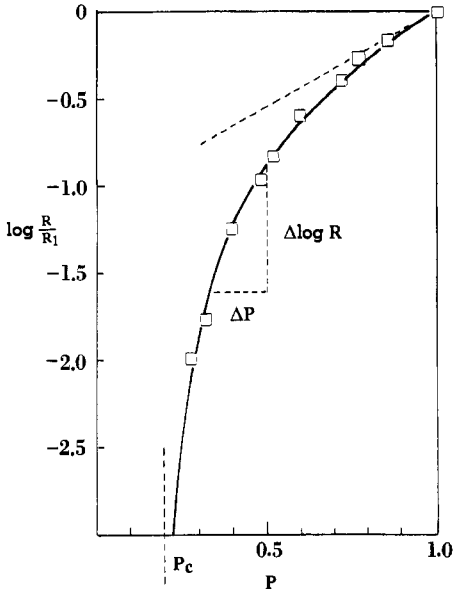


Figure 2. Semilogarithmic representation of the scaling law of percolative dissolution, $\log R = f(p)$. The experimental points refer to a series of partially methylated poly(4-hydroxystyrene) resins, group I, dissolving in 0.20 N KOH.

the phenols. We have modulated the percolation parameter of novolak, and of other phenolic resins, by progressively methylating their OH groups. The experimental points in Figure 2 refer to a series of partially methylated poly(4-hydroxystyrene) resins (group I). The composition of the individual members of the group is characterized by the fraction, x, of the original OH groups that are still free, i.e., have *not* been methylated. The derivation of the percolation parameter (p) from resin composition (x) is described in ref 7.

When an inhibitor is added to a resin, it blocks some of the OH groups[8,9] and thereby removes them from the percolation field. In this respect inhibitors act in a way similar to that of methylation; both lower the percolation parameter of the system. It is reasonable to assume that a change in p brought about by an inhibitor will be proportional to its concentration (c_i). For small quantities, dc_i, this leads to a relation between the inhibition factor and the slope $d \log R/dp$ of the scaling law plot of Figure 2.

$$f_{ij}(p) = -\frac{d \log R}{dc_i} = \alpha_i \frac{d \log R}{dp} \qquad (3)$$

In a group of related resins, the proportionality constant α_i depends only on the inhibitor (i).

The absence of a constant term in eq 3 implies that the inhibition factor extrapolates to the origin of the coordinates, $f_{ij} = 0$; $d \log R/dp = 0$. We have confirmed this for some strongly inhibiting additives (see Figure 3). However, in many other cases f_{ij} does not extrapolate to the origin, although a linear relation between f_{ij} and the slope $d \log R/dp$ is still maintained. We now introduce as a reference point the inhibition factor $f_{ij}°$ of the (unmethylated) base resin and replace eq 3 by eq 4.

$$f_{ij} - f_{ij}° = \alpha_1 \left[\frac{d \log R}{dp} - \frac{2 \log e}{1 - p_c} \right] \qquad (4)$$

(The percolation threshold, p_c, is that value of the percolation parameter below which dissolution no longer occurs. The last term in eq 4 is obtained by derivation of eq 2.) This formulation acknowledges that the extrapolation to $p \rightarrow \infty$ is rather distant and that, furthermore,

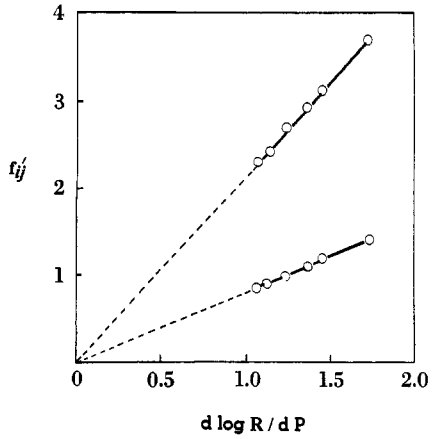
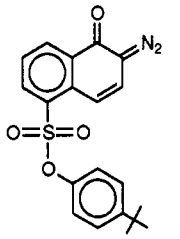


Figure 3. Inhibition factor (weight percent) plotted against the slope of the master curve of Figure 2. The data refer to the inhibitors α-naphthoflavone and octahydrobenzopyrenone in the resins of group III.

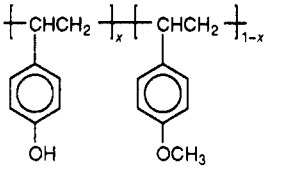
systems beyond the parameters of the base resin ($x = 1$, $p = 1$) cannot be experimentally realized.

Using the 4-*tert*-butyl ester of 2,1-naphthodiazoquinone-5-sulfonic acid as our standard inhibitor,

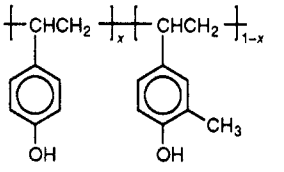


we have tested eq 4 on three types of resins.

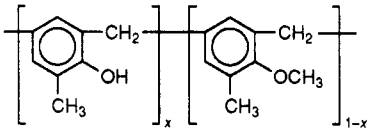
(I) Partially methylated poly(hydroxystyrene) resins



(II) Copolymers of 4–hydroxystyrene and 3–methyl–4–hydroxystyrene



(III) Partially methylated novolak resins made from 90% *o*-cresol and 10% *p*-cresol (or 85% *o*-cresol and 15% *p*-cresol in group IIIa).



The inhibition factor of the standard inhibitor was determined for all the resins of the three groups. The results are shown in Figure 4 where f_{ij} is plotted as a function of $d \log R/dp$. In agreement with eq 4, linear plots are obtained, but, unexpectedly, each plot consists of two branches separated by a discontinuity. What is the significance of this discontinuity? We believe that it signals a change in the state of the penetration zone, of that thin layer at the interface between the resin and developer solution which controls the diffusion of base

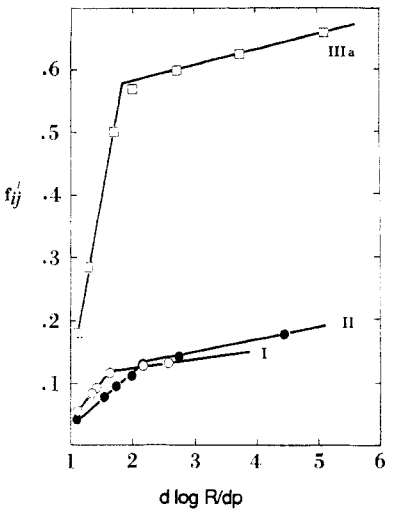


Figure 4. Inhibition factor (weight percent) of the standard diazoquinone inhibitor plotted as a function of d log R/dp for three series of phenolic resins. I is a group of partially methylated poly(4-hydroxystyrene), II is a series of copolymers of 4-hydroxystyrene and 3-methyl-4-hydroxystyrene, and IIIa is a group of resins based on a novolak made from 85% o-cresol and 15% p-cresol and partially methylated.

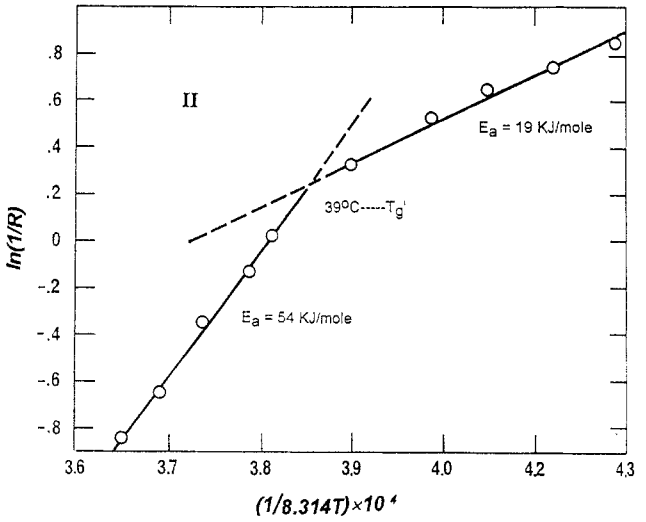


Figure 5. Arrhenius plot of the temperature dependence of the dissolution rate of a 1:1 copolymer of 4-hydroxystyrene and 3-methyl-4-hydroxystyrene, dissolving in 0.2 N KOH.

into the solid matrix.[2] The temperature at which the discontinuity occurs is the glass transition temperature of the penetration zone.

Glass Transition of the Penetration Zone

When a novolak film is immersed in aqueous alkali (the developer), base enters the matrix and converts some of the phenols into phenolate ions.

$$POH + K^+OH^- \rightleftharpoons PO^-K^+ + H_2O$$

At some point the solubility of phenolate in the resin is exceeded and, as Arcus[10] has shown, a new phase is formed at the interface with the developer solution, which he called the "membrane" and we call the penetration zone.[2]

As a well-defined polymeric phase, the penetration zone is characterized by a glass transition temperature, T_g'. The glass transition temperature of the penetration zone cannot be measured by calorimetry, but it can be inferred from the temperature dependence of the dissolution rate. Figure 5 shows an Arrhenius plot of the dissolution rate of a typical amphiphilic resin, an equimolar copolymer of

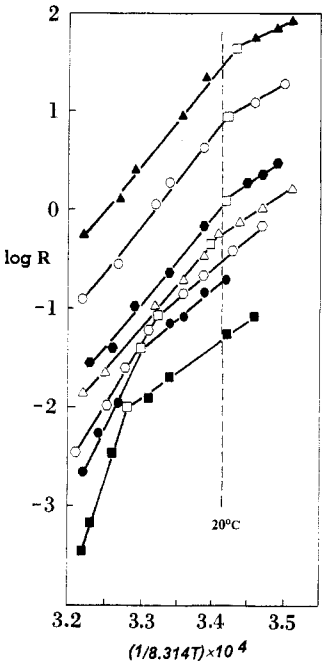


Figure 6. Arrhenius plot of the temperature dependence of the dissolution rate for the resins of group III.

4-hydroxystyrene and 3-methyl-4-hydroxystyrene. The plot has two branches that intersect at 39 °C, which, we believe, is the glass transition temperature of the penetration zone. That view is supported by earlier work of Huang et al.,[11] who observed a similar discontinuity in the temperature dependence of the dissolution rate in various other novolak derivatives. Above the temperature of the discontinuity the dissolution rate closely follows the WLF equation,[12] an expression which applies specifically to polymers above their glass transition temperature. That the glass transition has a significant effect on transport phenomena in membranes was recently observed by Kwei et al.,[13] who studied the permeability of various polymeric membranes to methane and found a break in the temperature dependence of permeability at the glass transition temperature of the membrane materials.

Methylation of the base resin usually lowers the intermolecular forces in the solid material, and, as a result, the glass transition of the dry resin and the glass transition of the penetration zone decrease. When T_g' falls below room temperature, the penetration zone enters a different viscoelastic regime and responds differently to the presence of inhibitor during development. That, we believe, is the reason for the discontinuity in the f_{ij} vs d log R/dp curves of Figure 4.

To show that the discontinuity in the f_{ij} vs d log R/dp plot in Figure 4 is linked to T_g', we have determined the glass transition temperature of the penetration zone for all the methylated novolak resins of group III, by measuring the temperature dependence of their dissolution rate. Figure 6 shows Arrhenius plots of some of the data. As the degree of methylation of the resin increases, the cohesion in the material becomes weaker and T_g' decreases. The break in the f_{ij} plot of Figure 4 corresponds to a resin with T_g' = 20 °C, which is the temperature at which the inhibition factors of Figure 4 were measured.

The discontinuity in the Arrhenius plot of Figure 5 indicates a profound change in the mechanism of base diffusion. Below the glass transition, the hydrophilic sites (the OH groups) are fixed in their locations, and only sites separated by very short distances will take part in the percolation process. In this situation the distribution of open bonds is independent of time and the activation

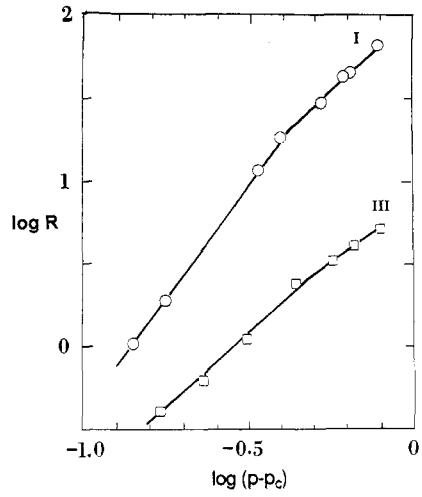


Figure 7. Double-logarithmic plot of the scaling law of percolative dissolution for the resin groups I and IIIa of Figure 4.

energy (4.54 kcal/mol) corresponds to the average energy barrier between two adjacent sites. Above the glass transition of the penetration zone, the hydrophilic sites become mobile, the environment of any site changes with time, and the number of potential site adjacencies (open bonds) increases dramatically. Site diffusion becomes now the rate-determining step, and the activation energy of the dissolution process (12.9 kcal/mol) is associated with the movement of the sites. Below T_g' the diffusant percolates in a field of stationary sites. Above T_g' the sites become mobile and cooperate in the diffusional transport.

Percolation in a Field of Mobile Sites

How does percolation in a field of mobile sites differ from percolation in a static field? That depends on whether all sites are identical or not. The effect of site motion on the value of the percolation parameter is probably quite small. When the sites become mobile, some site pairs which had formed open bonds in the static field will drift apart (and those bonds will disappear), but other sites will drift toward each other and new open bonds will be formed. The average number of open bonds ultimately depends on the overall site density, and that is the same in a mobile and in a static system. In a field of identical (undistinguishable) sites, the rate of dissolution depends almost entirely on the site density. The value of the percolation parameter (the fraction of open bonds) may somewhat fluctuate in the mobile system, but its time average will be constant. One would, therefore, expect that the rate of dissolution remains almost unaffected by the change from a static to a mobile percolation field.

That expectation is borne out by experiment. In earlier communications[4,7] it was found that in plotting log R against log($p - p_c$) the experimental points could be arranged on or around a straight line with a slope of 2. When we revisited the data, closer inspection revealed a slight discontinuity at the composition at which a discontinuity had been so clearly indicated in Figure 4. This can be seen in Figure 7 where we have plotted the data for the resins of group I and of group III. A discontinuity is discernible, but for all practical purposes the statements made in the earlier papers remain valid.

The situation is quite different in the presence of an inhibitor. In that case the sites are no longer identical. Some of them are now marked (blocked) by the inhibitor, while others remain free. In the static system, the blocked sites affect the dissolution rate by being located in the diffusional path, i.e., forming part of an infinite cluster. When the sites become mobile, site configurations around the blocked site change, and changes that remove the blocked site from the diffusional path will reduce the inhibition effect. That will happen in the majority of configurational rearrangements, because the blocked sites are in a minority, and it is more likely that a blocked site is replaced by a free site than the other way around. A more quantitative insight into this situation can be gained from a consideration of the proportionality constant α_i in eqs 3 and 4.

Percolation Cell Volumes and the Hydrophobic Displacement Volume of the Inhibitor

To interpret the proportionality constant α_i in molecular terms, the inhibitor concentration must be expressed in molar units, e.g., in moles per liter. In microlithographic practice inhibitor concentrations are usually expressed in weight percent, and in that case the molar inhibition factor f_{ij} is given by

$$f_{ij} = -\frac{\mathrm{d}\log R}{\mathrm{d}c_i} = -\frac{M_i}{10 d_j}\frac{\mathrm{d}\log R}{\mathrm{d}w_i} \tag{5}$$

where w_i is the weight fraction of inhibitor in the resin, d_j is the density (specific gravity) of the resin film, and M_i is the molecular weight of the inhibitor.

Let us now look upon methylation as a type of inhibition and consider the change in the percolation parameter p caused by a small additional quantity of methyl groups, $\mathrm{d}c_{CH_3}$. If the number of OH groups in the unit volume of the (partly methylated) resin j is n_j and the number of OH groups in the (nonmethylated) base resin is n_1, the fraction of free OH groups in resin j is $x = n_j/n_1$. It will be assumed that every additional methyl group blocks *one* OH group of the resin, causing a change $\mathrm{d}n$ in the number of free OH groups.

$$\mathrm{d}n = \mathrm{d}n_j = -\mathrm{d}c_{CH_3} = n_1\,\mathrm{d}x \tag{6}$$

It was shown in ref 7 that, in a group of related resins, p is a linear function of x.

$$p = ax + (1 - a),\quad \mathrm{d}x = (1/a)\,\mathrm{d}p,\ \mathrm{d}c_{CH_3} = -(n_1/a)\,\mathrm{d}p \tag{7}$$

Introducing eq 7 into eq 1, one obtains what might be called the "inhibition factor" of CH_3 groups introduced into the resin on methylation.

$$f_{CH_3} = -\frac{\mathrm{d}\log R}{\mathrm{d}c_{CH_3}} = \frac{a}{n_1}\frac{\mathrm{d}\log R}{\mathrm{d}p} \tag{8}$$

The factor a/n_1 in eq 8 has a simple physical meaning: it represents the volume of 1 mol of percolation cells. For example, in the resins of group III, a/n_1 = 2.65/10.8 = 0.2454 L/mol = 245.4 mL/mol. The volume of a single percolation cell can be obtained from this by dividing with Avogadro's number. For the resins of group III the single percolation cell volume is 407 Å^3. If the percolation cells are thought of as cubes, their linear dimension (the cube edge) is s = 7.4 Å.

The ratio a/n_1 is not exclusively linked to methylation; it represents quite generally the molar volume of the percolation cells in amphiphilic systems. These systems are comprised of groups of resins of related structure, the members of which are distinct from each other only by a small, well-defined compositional change. In groups I and III this change is the replacement of a phenol by a

methoxyphenol, in group II it is the change from a freely accessible phenol to one partly hindered by a methyl group in the ortho-position of the phenyl ring. In yet other resins it is a change in the ratio of *p*-cresol and *m*-cresol units. These changes (methylation and steric hindrance) introduce islands of hydrophobicity at or near the hydrophilic site, and it is the presence of these hydrophobic domains that causes the observed lowering of the dissolution rate.

While the volume of percolation cells is commonly in the range between 200 and 1000 Å^3, practical inhibitors import much larger hydrophobic domains into the system. Their volume is measured by the proportionality constant α_i, which is the slope of a plot of f_{ij} (in molar units) against d log R/dp. This slope has the dimension of a molar volume, and it represents the space in the percolation zone in which the inhibitor has effectively disabled the hydrophilic sites and made them unavailable to the percolation process. Because the hydrophilic percolation sites have been quasi displaced from that space, it will be called the "hydrophobic displacement volume" of the inhibitor. If f_{ij} is measured in terms of weight percent, the slope of the f_{ij} vs d log R/dp plot may be converted into the hydrophobic displacement volume by using the molecular weight of the inhibitor and the density (specific gravity) of the resin film in the following formula.

$$\alpha_i = \text{slope} \times (M_i/10d_j) \tag{9}$$

The slope of the line for the standard inhibitor in the resins of group III is found to be 0.55 in Figure 4. With M_i = 396 and d_j = 1.30 for the resins of group IIIa, the hydrophobic displacement volume of the inhibitor becomes α_i = 0.55(396/13.0) = 16.8 L/mol of inhibitor. This corresponds to a hydrophobic displacement volume of 26 700 Å^3 for a single inhibitor molecule.

Hydrophobic Displacement Volume in Different Resins

The hydrophobic displacement volume is not only a characteristic of the inhibitor but it depends also on the nature and the physical state of the resin. This can be demonstrated by introducing the standard diazoquinone inhibitor into the three types of resins shown in Figure 4. For the resins of group IIIa with T_g' *above* room temperature we found a hydrophobic displacement volume of α_1 = 16.8 L/mol or 26 700 Å^3, corresponding to a linear dimension (cube edge) of 29.9 Å. In the resins that have T_g' *below* room temperature, the hydrophobic volume, as derived from the slope of the second part of the plot in Figure 4, is only α_i = 0.73 L/mol or 1212 Å^3, corresponding to a linear dimension of 10.7 Å. We believe that this large difference is caused by the change in the percolation mechanism that occurs at T_g'. Above the glass transition of the penetration zone the percolation sites are mobile, and new site configurations are spontaneously formed in the surroundings of the inhibited site. These transient new configurations allow the diffusant to circumnavigate the blocked site. In a field of mobile sites the inhibitor represents now much less of an obstacle to percolation, and its hydrophobic displacement volume, i.e., the volume made unavailable to percolation, is much smaller.

The change that occurs at the glass transition temperature of the penetration zone suggests also an explanation for the well-known difference in the dissolution behavior of novolak and of poly(vinylphenol). A quantity of inhibitor that will lower the dissolution rate of novolak by a factor of 10 will change the dissolution rate of poly(vinylphenol) only by a factor of 2 or 3. This difference is clearly reflected in the hydrophobic volume of the standard inhibitor in the two resins. For example, *below* T_g', the hydrophobic displacement volume of the generic diazoquinone inhibitor in the resins of group I (partly methylated poly(vinylphenol)) is α_i = 3.36, about one-fifth of its value in group IIIa. We believe that this difference is caused by the motion of the side chains in poly(4-hydroxystyrene). Side-chain motion is still active at room temperature and stops only at the γ point, which, for polystyrene, has been reported between −141 and −73 °C.[14,15] The data on the behavior of the standard diazoquinone inhibitor in the three groups of resins are collected in Table 1.

Table 1. Hydrophobic Displacement Volume of the Standard Inhibitor in Different Types of Resin

resin group	a[a]	α_1[b] below T_g' L/mol	Å^3	s (Å)[c]	above T_g' L/mol	Å^3	s (Å)[c]
I	2.86	3.36	5610	17.8	0.39	647	8.65
II	2.53	2.53	4200	16.1	0.56	930	9.76
III	3.00	15.5	25700	29.9	0.73	1200	10.7

[a] a is the correlation constant linking p to x (see eq 7). [b] α_i is the hydrophobic displacement volume, in (L/mol), and in the adjacent column it is given in Å^3. [c] s is the linear dimension (cube edge) of the molecular hydrophobic displacement volume.

Table 2. Percolation Characteristics of Group III Resins

x[a]	R (μm/min)[b]	log R	p[c]	d log R/dp	T_g'[d]
1.00	21	1.322	1.00	1.075	31.7
0.985	18.9	1.276	0.960	1.132	30.0
0.956	16.3	1.212	0.884	1.27	28.2
0.935	13.5	1.130	0.828	1.37	25.6
0.915	11.0	1.041	0.762	1.47	23.7
0.885	8.36	0.922	0.695	1.74	21.0

[a] x is the fraction of free OH groups. [b] R is the dissolution rate of μm/min. [c] $p = 2.65x - 1.65$. [d] Tg' is the glass transition temperature of the penetration zone, a/n_1 = 0.245 L/mol; the percolation cell volume is 407 Å^3.

Hydrophobic Displacement Volumes of Different Inhibitors

To demonstrate the usefulness of the concept of a hydrophobic displacement volume in characterizing the performance of an inhibitor, we have determined the inhibition effect of 10 different inhibitors in those resins of group III which have T_g' above 20 °C, the temperature at which the dissolution measurements were made. The percolation characteristics of this group of resins are listed in Table 2. The inhibitors to be used were so chosen as to present a gradation of molar volumes and hence, presumably, of hydrophobic displacement volumes. The results are shown in Figure 8 where we have plotted the inhibition factors against the values of d log R/dp. It can be seen that in all cases linear plots are obtained. From their slope the hydrophobic displacement volumes of the inhibitors may be calculated. These data, together with the inhibition factors $f_{ij}°$ of the inhibitors in the unmethylated base resins, are collected in Table 3.

Values of $f_{ij}°$ are plotted as a function of the hydrophobic volumes in Figure 9, and it can be seen that the two quantities are linearly related. The slope of the correlation line may be derived from eq 10.

$$f_{ij}° = \alpha_i \frac{\text{d log } R}{\text{d}p} = \alpha_i \frac{0.869}{1 - 0.20} = 1.086\alpha_i \tag{10}$$

If α_i is expressed in molecular units (Å^3), the proportionality constant has to be multiplied by Avogadro's number, leading to the relation

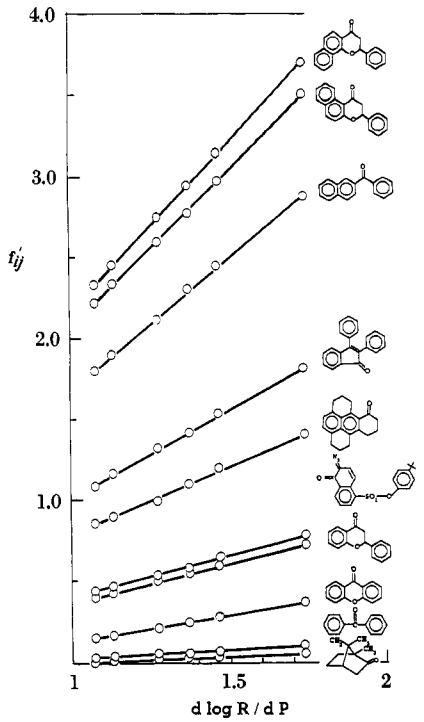


Figure 8. Inhibition factors (weight percent) of a number of inhibitors incorporated in the resins of group III, plotted as a function of d log R/dp.

Table 3. Inhibition Factors and Hydrophobic Displacement Volumes of Inhibitors in Resins of Group III

				α_i[e]		
no.	inhibitor	f_{ij}°[a]	M_i[b]	L/mol	Å^3	s (Å)[d]
1	(*S*)-camphor	0.11	152	0.20	332	6.9
2	benzophenone	0.55	237	2.55	4 230	16.2
3	xanthone	2.26	196	5.13	8 520	20.4
4	flavone	6.80	222	8.88	14 740	24.5
5	standard diazoquinone	13.1	396	16.8	26 700	29.7
6	octahydrobenzopyrenone	18.3	276	18.5	30 700	31.3
7	2,3-diphenylindenone	23.6	282	23.6	39 200	34.0
8	2-benzoylnaphthalene	32.0	231	29.5	48 900	36.6
9	β-naphthoflavone	46.6	273	38.5	64 000	40.0
10	α-naphthoflavone	49.1	273	45.8	76 000	42.4

[a] f_{ij}° is the inhibition coefficients of the additive in the base resin. [b] M_i is the molecular weight of the inhibitor. [c] α_i is the hydrophobic displacement volume, in L/mol; in the next column it is given in Å^3. [d] s (Å) is the linear dimension (cube edge) of the hydrophobic displacement volume. The correlation constant linking p and x for the resins of group III is $a = 2.65$. The volume of the percolation cells in the resins of group III is 407 Å^3.

$$f_{ij}^{\circ} = 65.44 \times 10^{-8}\alpha_i \text{ (Å}^3\text{)} \qquad (10a)$$

The factor 65.44×10^{-8} is the slope of the line indicated in Figure 9. The experimental points of most systems are not too far removed from this simple correlation.

The hydrophobic displacement volume is not easily estimated from the structural formula of an additive, and molar volumes calculated by various approximate methods are often misleading. The results in Table 3 show that in this context small structural changes can play a disproportionately large role. We refer, e.g., to the difference in the displacement volumes of flavone and naphthoflavone, diphenyl ketone (benzophenone), and naphthyl phenyl ketone (benzoylnaphthalene).

Conclusions

The existence of the discontinuities in the plots of Figure 4, which we have linked to the glass transition of the penetration zone, supports Arcus'[10] prediction that base diffusion through the penetration zone is the rate-controlling step in novolak dissolution. Base diffusion in these systems is a percolation process; in the amphiphilic novolak matrix ions migrate by transferring from one hydrophilic site to the next.

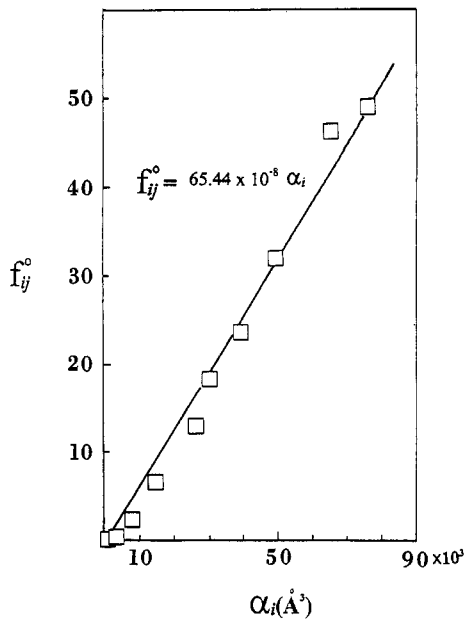


Figure 9. Correlation between the hydrophobic displacement volume α_i of an additive and its inhibition factor f_{ij}° in the base resin of group III.

Inhibitors function by blocking some of the percolation sites, thereby obstructing diffusional pathways. In so doing they create hydrophobic domains in the resin matrix where the hydrophilic sites have been either disabled or displaced, at any rate made unavailable to the percolation process. The hydrophobic displacement volume associated with 1 mol of inhibitor is the fundamental molecular characteristic of an additive, its figure of merit as a dissolution inhibitor. The hydrophobic displacement volume is given by the proportionality constant α_i in eqs 3 and 4.

The hydrophobic displacement volume depends not only on the molecular structure of the inhibitor but also on the nature and the viscoelastic state of the resin matrix. It is much larger below the glass transition of the penetration zone, and it is generally lowered by any kind of molecular motion in the matrix. This we believe is the reason for the comparative poor inhibitability of poly(vinylphenol) and its derivatives as compared with novolak resins.

Experimental Part

Materials. The resins of group I were prepared by partially methylating a single batch of poly(4-hydroxystyrene), MW 22 000 (Polysciences). Details are in ref 4. The resins of group II were obtained from the laboratory of Hoechst AG in Frankfurt; their synthesis is described in ref 16. The novolak resins were prepared by the condensation of cresols with formaldehyde. A melt of *o*-cresol (1200 g) was added to a 3-L round-bottomed flask which contained 60 g of *p*-cresol and 760 g of formaldehyde (in a 37% aqueous solution). *p*-Toluenesulfonic acid monohydrate (20 g) was added as a catalyst, and the mixture was heated to 100 °C and refluxed for 5 h. The polymer precipitated and, after cooling, was separated from the water phase and heated in a vacuum (180 °C/3 mmHg). It was then dissolved in acetone and reprecipated into water, and that procedure was repeated three times. The final product was dried in a vacuum oven (90 °C/3 mmHg). The product, obtained in 80% yield, is a light orange powder, M_w 2500 (GPC, polystyrene calibration).

The resins of group II were described in ref 16. The novolak resins of group III were partially methylated with dimethyl sulfate. The novolak resin (100 g, 0.82 mol) was dissolved in 800 mL of

a 10% aqueous solution of KOH, and 1.5 mL (0.015 mol) of dimethyl sulfate was added. After refluxing under nitrogen for 30 min, the solution was poured into acidic water to neutralize the KOH. The precipitate was dissolved in acetone, and the solution was filtered and reprecipitated into water. This procedure was repeated twice. The final product was dried at 90 °C (3 mmHg) overnight. The yield was 70%, based on the methylated phenol groups. A series of partially methylated resins was prepared by increasing the quantity of dimethyl sulfate. The fraction of free (unmethylated) OH groups was estimated from proton NMR. The sample was dissolved in acetone-d_6 and the NMR spectrum measured with a Varian EM 390 spectrometer. The integrated signal of the OH protons was calibrated on the internal standard of the protons of the phenyl ring. A group of increasingly methylated derivatives of the standard novolak resin (90% *o*-cresol and 10% *p*-cresol) was prepared as a test system for the inhibitors of this study. The properties of this group of resins are listed in Table 2.

The generic diazoquinone inhibitor, the *tert*-butylphenyl ester of 1,2-diazonaphthoquinone-5-sulfonic acid, was kindly supplied to us by Dr. Trevor Clarke of St. Jean Photo Chemicals, Inc. The other inhibiting additives were obtained from Aldrich Chemical Co.

Dissolution Rate Measurements. The resins containing varying quantities of inhibitors were spin coated onto silicon wafers, dried, and prebaked at 90 °C for 1 h. They were then immersed in 0.2 N aqueous KOH, and the rate of dissolution was measured by laser interferometry, as described in ref 7. The data were evaluated by the method of Rodriguez et al.[17]

Determining the Percolation Parameter in a Group of Resins. The percolation parameter, p, is a linear function of the fraction, x, of free OH groups in the resin. The correlation constant a which links the two variables is determined as described in ref 7, p 3865. For the group of test resins (IIIa) used in this study it has the value $a = 2.65$.

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