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A New Design Principle for the Photoactive Components (PACs) of Dissolution Inhibition Resists

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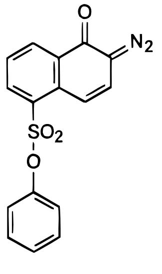
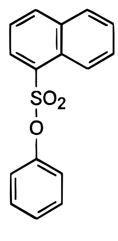
ABSTRACT: The photoreactive function and the inhibitor function of the Photoactive components (PACs) of dissolution inhibition resists are independent of each other and have to be considered and developed separately. Traditionally, dissolution inhibitors have been designed by trial and error. Here we are concerned with a rational approach to inhibitor design based on the proposition that the inhibition strength of a molecule depends directly on the electron density on the oxygen atom of its acceptor group. Any structural change that increases the electron density on the acceptor increases also the inhibition factor of the molecule. Several routes to more effective inhibitors are indicated.

Introduction

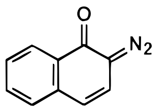
The photoactive components (PACs) of traditional Novolak resists are esters of diazonaphthoquinone (DNQ) sulfonic acid.[1,2] A typical example is shown in structure **A**. For a long time it was thought that the essential function of the PAC is centered in its DNQ moiety and that the sulfonic acid is only a convenient means of linking the DNQ to various aromatic balast groups. This view changed when Murata et al.[3,4] showed that the sulfonyl ester **B** is almost as effective an inhibitor as **A** and that the unsubstituted diazonaphthoquinone **C** is only a poor inhibitor.



A



B



C

Honda and others[5,6] confirmed later that the two functions of the PAC are realized by different parts of the molecule. The photoreactive function is clearly associated with the DNQ moiety, while the inhibitor function is vested mainly in the SO_2 group. The two functions are independent of each other in the sense that the presence of the inhibitor group does not affect the quantum yield of the photoreaction of the DNQ and vice versa. This being the case, the two functions may be considered, and developed, separately. Here we shall be concerned with the inhibitor function.

The inhibition strength of a compound is characterized by an inhibition factor, *f*, which is defined as the negative slope of a plot of log *R* against the inhibitor concentration in the resist film (a so-called Meyerhofer plot).[2,7]

$$\mathrm{f} = -\frac{\mathrm{d}(\log R)}{\mathrm{d}c_{\mathrm{i}}}$$

Here *R* is the dissolution rate (e.g., in A/s) and c_i is the concentration of inhibitor in the resist film. We have used mol % (moles of inhibitor in 100 g of Novolak) as a measure of concentration. Figure 1 shows the Meyerhofer plot of a typical commercial PAC in Novolak.

In searching for a rational approach to the design of dissolution inhibitors we have to answer two questions:

1. What property decides the inhibition strength of a molecule?
2. How can we optimize that property by manipulating molecular structure?

Which Property of the Molecule Controls Inhibition Strength?

In terms of the percolation model of Novolak resists we believe that inhibitors function by forming a hydrogen bond with a nearby OH group of the phenolic resin. In so doing they polarize the OH bond, the oxygen atom of which becomes a better hydrogen acceptor than the OH groups in the bulk of the resin. The polarized group forms another hydrogen bond with the next phenol, and that in turn interacts with the next, and so on. A "phenolic string" is formed in the coating solution which survives into the dry resist film. The protons of the OH groups in a string are bonded, albeit not equally, to *two* oxygen atoms and are therefore less available for interaction with base than the protons of the groups in the bulk of the resin. This slows down the progress of base during development, and that in turn lowers the dissolution rate.

It follows from the foregoing that the inhibition strength of a molecule depends on its ability to interact by hydrogen bonding with the OH groups of the resin, and we have demonstrated this in an earlier com-

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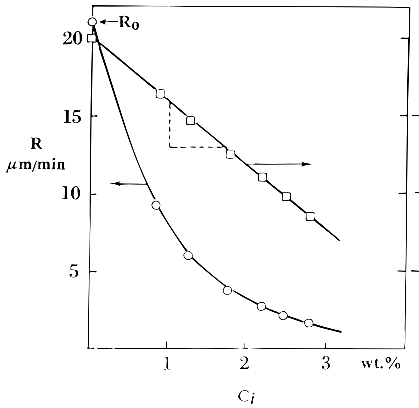
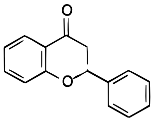


Figure 1. Meyerhofer plot of a typical PAC. The negative slope of the logarithmic plot defines the inhibition factor *f*.

munication.[8] The question arises: which molecular property controls the hydrogen-bonding propensity of the inhibitor? From first principles one would expect it to be the electron density at the oxygen atom of the acceptor.[19]

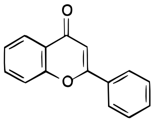
Earlier we had come across a group of three pyrones which seemed to make this point. Although these molecules have very similar structures, they differ sharply in their ability to inhibit the dissolution of Novolak. The group is well suited for a test of the above proposition.



E

flavanone

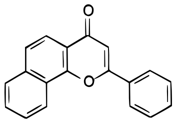
f = 6.8



F

flavone

f = 18



G

α-naphthoflavone

f = 49

The dipole moment of carbonyl is the result of differences in the electron affinities of the two atoms. It can realize itself more fully when the electrons of an aromatic system are made available to it. In flavanone a single benzene ring is linked to the carbonyl, in flavone the phenyl ring in the 3-position of the pyran ring is connected to the acceptor group through the double bond in the heterocycle, in naphthoflavone another benzene ring is added. We have calculated the electron densities on the carbonyl oxygen of the three compounds using an advanced MNDO program.[10−13] The results in Figure 2 support the qualitative statement of the previous paragraph.

The relation between electron density (basicity) and inhibition strength is so fundamental to the design of dissolution inhibitors that we thought it should be confirmed on a somewhat larger database. For that purpose we chose a group of aromatic ketones. We calculated the electron densities on the oxygen atom of the carbonyl, and measured their inhibition factors. Some of the compounds were obtained from outside suppliers, others we synthesized ourselves. The experimental data are listed in Table 1. The plot in Figure 3 confirms the linear correlation between electron density and inhibition.

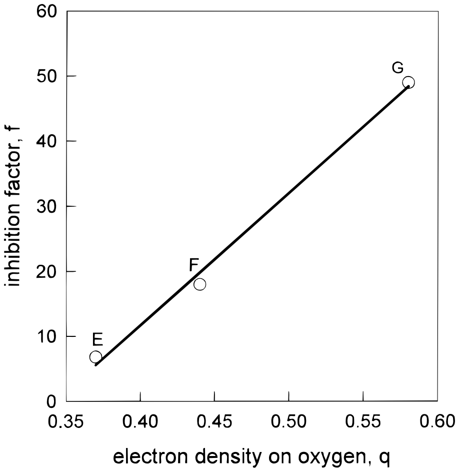


Figure 2. Correlation between electron density on the acceptor carbonyl and inhibition. strength in a group of three pyrones.

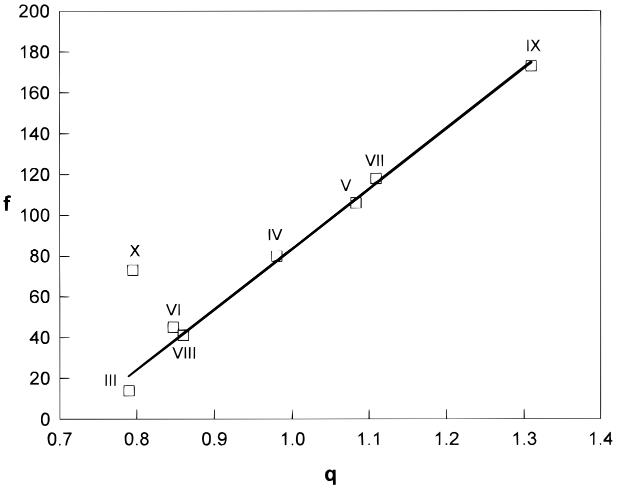
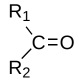


Figure 3. Correlation between electron density on carbonyl and inhibition strength in a group of aromatic ketones, as indicated in Table 1.

Table 1. Charge Densities, *q*, on Carbonyl Oxygen, and Inhibition Factors, *f*, for a Group of Aromatic Ketones



$$R_1R_2C{=}O$$

	R_1	R_2	*q*	*f*
I	H	H	−0.145	
II	H	Ph	0.216	
III	Ph	Ph	0.790	14
IV	Ph	1-naphthyl	0.980	80
V	Ph	2-naphthyl	1.083	106
VI	1-naphthyl	1-naphthyl	0.847	45
VII	Ph	4-diphenyl	1.109	118
VIII	1-naphthyl	9-anthryl	0.860	41
IX	Ph	2-anthryl	1.309	173
X	Ph	9-anthryl	0.795	73

We have recently become aware of the work of Christopher McAdams, who pursued the same basic idea.[9] McAdams, a member of Professor Willson's group at the University of Texas at Austin was looking for a connection between the basicity (electron density) of inhibitors and their inhibition strength. In a very elegant experiment he demonstrated a linear correlation between the inhibition strength of various substituted benzophenones and their basicity, measuring the basicity of the carbonyl by the sum of the Hammett sigma constants of the substituents. Taking all these data together, we feel that the relation between electron

Table 2. Inhibition Factors of Substituted PACs

R	*f*
H	42
tert-butyl	45
CH_3	45
NO_2	41
bisphenol	40

density on the acceptor group and inhibition strength has been convincingly established.

Maximizing the Electron Density at the Acceptor Site

The origin of the dipole moment of the acceptor group is the difference between the electronegativities of two atoms. We list the electronegativies of some relevant atoms and their differences in atomic pairs as follows:

Electronegativities of Atoms

Si	P	S	C	N	O
1.74	2.06	2.44	2.50	3.07	3.50

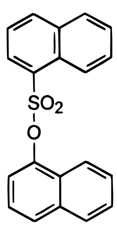
C=N	C=O	S=O	P=O
0.57	1.00	1.06	1.44

The C=N dipole is weak and will play almost no role in string formation. Judging by the electronegativity differences the sulfur-based inhibitors are somewhat more effective than the corresponding ketones, and that is in fact observed. The phosphorus–oxygen dipole would produce efficient inhibitors, but phosphorus is a strong dopant of silicon and is therefore not acceptable in the microlithography of silicon devices. In practice that means that valid dissolution inhibitors are based on derivatives of sulfonic acids or on ketones. How can the electron densities on the oxygen atoms of these two types of acceptors be increased. Three strategies may be followed: (1) Substitution; (2) reorganization of the immediate surroundings of the acceptor group; (3) increases in the size of the aromatic network connected to the acceptor.

1. Substitution. Substituent effects on inhibition strength are demonstrated most effectively in the work of McAdams.[9] By using both electron-withdrawing and electron-donating substituents, he was able to change the inhibition strength of substituted benzophenones within a range from 0.8 to 2.2 relative units, i.e., by a factor of 2.75. To achieve effects of this magnitude, it is necessary to link the substituents directly to the acceptor site.

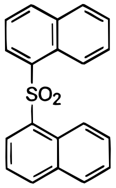
We have investigated the effect of substituents attached in the 4-position of the phenyl ring in PAC **A**. The results are listed in Table 2. Here the effect of substituents on the inhibition factor of the standard inhibitor is very small. We believe that this is caused by the phenolic oxygen which isolates the substituent from the acceptor site. As expected, exchanging H for a *tert*-butyl or a methyl group increases inhibition; the electron-withdrawing nitro- or bisphenolyl groups lower it. In any case, the changes are not significant.

2. Reorganization of the Surroundings of the Acceptor Group. In the standard sulfonate PAC the source of the partial charge on oxygen is the difference between the electronegativities of S and O. The charges on all the oxygen atoms are compensated by the inherent electronegativity of the sulfur atom; it should therefore be possible to increase the charge on the two double-bonded oxygens by removing the third oxygen of the sulfonic acid ester. We have tried this idea on the dinaphthyl compounds.



H

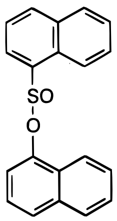
f = 51



J

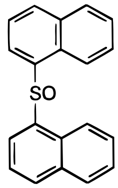
f = 86

The increase in the inhibition factors is substantial; it corresponds to a lowering of the dissolution rate by a factor of 50! In a further step we have tried to remove the second oxygen by going from the sulfate to the sulfinate and from the sulfone to the sulfoxide. Surprisingly, the inhibition factors remained unchanged. This means, we believe, that two identical phenolic strings issue from compounds **H** or **J**, while only one string emerges from the sulfinate **K** or the sulfoxide **L**, but that string has twice the length of the individual strings of the former.



K

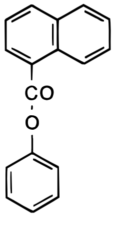
f = 50



L

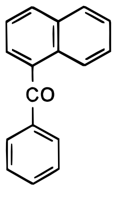
f = 87

An even stronger effect is observed when comparing the ester of a carboxylic acid **M** with the corresponding ketone **N**.



M

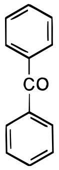
f = 3



N

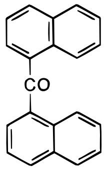
f = 32

3. Increasing the Size of the Aromatic System Connected to the Acceptor. The electron densitity on the acceptor group can be increased by making available to it electrons from a suitable reservoir. In practice that means that a larger aromatic system is connected to it. We had observed earlier that the size of the aromatic network connected to the acceptor dipole appears to play an important role. In going from diphenyl ketone to di(1-naphthyl) ketone the inhibition factor increases from a value of 14 to 45. The change from diphenyl sulfoxide to dinaphthyl sulfoxide is even more dramatic.



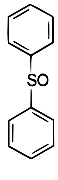
III

f = 14



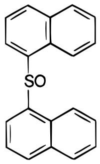
VI

f = 45



O

f = 19



L

f = 87

While the provision of large aromatics is a powerful means of increasing inhibition strength, it is not acceptable in optical microlithography where the complete bleaching of the PAC is a requirement. However, the high contrast achievable with larger aromatic inhibitors may be desirable in X-ray lithography and in electron beam lithography, as well as in the large scale applications of the digital printing industry.

In summary: The key to the design of powerful inhibitors is the maximization of the electron density on the oxygen of the acceptor group of the PAC. Some of the structural changes leading to this goal are compatible with the requirements of optical lithography; others may be useful in different applications. How this is achieved in practice will depend on a number of factors, not least on the imagination and the skill of the resist chemist.

Quantum Chemical Calculations

A Gaussian program package[10] was used throughout. The MNDO calculations[11,12] were based on the VSTO-3G(5D,7F) standard basis set. Atomic charges were fitted to the electrostatic potential of the molecules by the CHELPG scheme.[13] The calculated dipole moments were constrained to the correct values.

Experimental Section

Sample Preparation and Dissolution Measurements. The inhibitors were introduced in varying amounts into casting solutions containing 25 wt % of a commercial novolak in isoamyl acetate. Resist films were cast onto 2 in. diameter silicon wafers using a spinner at 3000 rpm. The dry wafers were kept at 90 °C for 1 h. They were then immersed in 0.2 N KOH solutions and their dissolution rate was measured with a single channel laser interferometer, which was described earlier.[14]

Materials. Compounds **E**, **F**, **G**, **N**, **III**, and **V** were purchased from Aldrich Chemicals, as well as all starting materials and solvents. Compounds **A** and **C** were graciously supplied by St. Jean PhotoChemicals of St. Jean-sur-Richelieu, Quebec, Canada, and compound **VII** in Table 1 was a gift of Christopher McAdams of the University of Texas, Austin. All other compounds were synthesized in this laboratory by standard methods. Four of the somewhat less routine preparations are described below. In all cases the identity of the final products was confirmed by their proton NMR and by their FTIR spectra.

Naphthalene-1-sulfonic acid 1-Naphthyl Ester,[15] H. This is a standard preparation in resist chemistry. We include it here for the sake of completeness. To a flame-dried 50 mL round-bottom three-neck flask equipped with a dropping funnel, gas adaptor, and rubber septum was added 1 g (6.93 mmol) of 1-naphthol dissolved in pyridine. To this was subsequently added a solution of 1-naphthylsulfonyl chloride (1.57 g, 6.93 mmol) in 6 mL of pyridine. This solution was added dropwise to the reaction flask at a temperature of 0 °C. After the addition was complete, the flask was allowed to come to room temperature, and the contents were stirred overnight. The reaction mixture was then added to a HCl−ice−water mixture and finally extracted with ethyl acetate. The ethyl acetate solution was shaken with brine and then dried over magnesium sulfate overnight. It was evaporated to yield 1.70 g of a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ 6.9−9.04 (m, 14H).

Di-1-naphthyl Sulfone,[16] J. A flame-dried 250 mL round-bottom flask was equipped with a mechanical stirrer, reflux condenser, and gas adapter and charged with 7 g (0.0235 mol) of naphthalene sulfonic acid, 3.015 g (0.0235 mol) of naphthalene and 70 g of polyphosphoric acid. The mixture was stirred and then heated to 85° C for 8 h. After that, the viscous mixture was poured over ice−water and stirred overnight. The mixture was then filtered and washed with water. A light gray powder was obtained (6.0 g), mp 187.5 °C . ^{1}H NMR ($CDCl_3$): δ 7.3−8.78 (m, 14H).

Naphthalene-1-sulfinic acid 1-Naphthyl Ester,[17] K. A flame-dried 50 mL three neck round-bottom flask was equipped with a dropping funnel, gas adaptor, and a stirrer. It was charged with 1-naphthol 0.55 g, (3.78 mmol) dissolved in 10 mL of CH_2Cl_2. The solution was cooled to 0 °C, and then 1 mL of triethylamine was added. Subsequently, 0.86 g (3.78 mmol) of 1-naphthylsulfonyl chloride was added. This addition was made dropwise through a dropping funnel. When this was complete, 0.9 mL (0.94 g, 7.63 mmol) of trimethyl phosphite was added and the whole mixture was refluxed for 8 h. The reaction mixture was then poured into HCl−ice−water, and subsequently extracted with dichloroethane. The extract was dried over magnesium sulfate and then evaporated in a rotovap apparatus; 0.88 g of a whitish powder was obtained. Mp: 103 °C. ^{1}H NMR ($CDCl_3$): δ 6.5−9.04 (m, 14H).

Di-1-naphthyl Sulfoxide,[18] L. A flame-dried 50 mL three neck round-bottom flask was equipped with a dropping funnel, reflux condenser and septum. It was charged with 0.242 g (9.98 mmol) of magnesium, 10 mL of ether and 1.99 g (9.65 mmol) of 1-bromonaphthalene. The mixture was refluxed for 5 h and then cooled to 5° C. At this temperature there was added to the mixture 0.35 mL (0.564 g, 4.82 mmol) of $SOCl_2$ over a period of 1 h. The reaction mixture was allowed to come to room temperature and stirred for 3 h. It was then poured into ice−water in a 100 mL beaker. The ether layer was collected and dried over magnesium sulfate. It was evaporated to yield 0.54 g of a pale yellow powder. Mp: 166 °C. (lit. 165−166 °C). ^{1}H NMR ($CDCl_3$): δ 7.28−8.38 (m, 14H).

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(19) Strictly speaking, it should be the energy difference between the bound and the free form of the acceptor, but that can be shown (by perturbation methods) to be proportional to the electronic charge, *q*, on the oxygen.

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