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**CHARACTERIZATION AND MODELING
OF RESIST DEVELOPMENT
WITH SURFACTANTS**

by
Cynthia Zee

Memorandum No. UCB/ERL M88/11

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Acknowledgements

I would like to express my appreciation to Professor Neureuther for his support and patience throughout this work and to Professor Oldham for his helpful suggestions. Thanks also to the rest of the SAMPLE group, especially Bill Bell for developing the analysis software, FINDRM and PARMEX, and the staff in the Microfabrication Lab for their assistance.

Finally, I would like to thank my family for their support and encouragement.

Characterization and Modeling of Developers

Abstract

The effects of various developers on resist dissolution are explored using the Perkin Elmer Development Rate Monitor (DRM) with matched substrates and increased agitation. A thin-film stack of nitride/oxide/nitride was designed using simulation and reduced the reflectivity to less than 1% at the measurement wavelength of 436nm. The three layer coating was fabricated using standard IC processing and the low reflectivity was verified by direct measurement on a Perkin- Elmer UV/VIS spectrophotometer.

The dissolution of Shipley 1400-31 resist in three commercial developers with and without agitation was quantitatively characterized. MF314 with agitation shows by far the highest contrast and sensitivity with agitation. MF319 shows improved contrast over MF312 for immersion type development but does not have nearly the high contrast of MF314 with agitation. The contrast for both MF312 and 319 is less affected by agitation. Potassium hydroxide with FSC surfactant shows similar behaviour to MF314 but significant foaming occurs.

Finally, the experimental data is analyzed using auxillary software to plot dissolution rate R versus exposure state M . The $R(M)$ plots characterization approach allows surface rate retardation effects to be clearly distinguished from basic resist contrast. Resist profiles are also simulated using SAMPLE.

1.0 Introduction

The increasing complexity of lithographic process requires the balance of many "tradeoffs" in optimizing the exposure, resist and developer materials and processing conditions. Quantitative models and simulations are useful for understanding these "tradeoffs". Although the Perkin Elmer Development Rate Monitor is available to relieve some of the difficulties in obtaining quantitative models, the data obtained is subject to noise problems. Section 2 describes the techniques used to improve these measurements.

The role of developers in resist dissolution is still not well understood. For this reason, the variations in performance of a given resist is explored as a function of three commercial developers. Measurement data and models for use with SAMPLE are given in Sections 3 and 4. A similar study with potassium hydroxide and surfactants is presented in Section 5.

2.0 Measurement Techniques on the DRM

Accurate measurement of resist development on the DRM in the past has been limited by the lack of agitation in the tank as well as the presence of standing waves in the photoresist. Two approaches are investigated to improve the quality of the results:

1. increasing the agitation in the development tank, and
2. the use of matched substrates to minimize reflections.

2.1 DRM flow modifications

The original flow distribution system on the DRM (shown in Figure 2.1a) provides very little circulation in the tank because the developer is pumped into and out of the tank on the same side. Byproducts of the development do not get removed from the wafer surface and degrade the intensity of the zone signal resulting in the bow shaped curve shown in Figure 2.2a. Transport of fresh developer to the wafer is also inhibited, causing the development process to become diffusion limited. In order to ensure that the development is surface reaction-rate controlled, a flow rate of over 10cm/sec has to be achieved.

The equipment is modified to provide greater agitation. A pump with great capacity and a manifold-type distribution system (Figure 2.1b) are installed. The sideports on the manifold direct fresh developer continuously over the wafer surface and a velocity of over 100cm/sec is obtained. Figure 2.2b shows that both the zone signal and the development rate are improved.

2.2 Design of Matched Substrates

When monochromatic light is used for exposure, standing waves occur in the photoresist because light is reflected back from the substrate and interferes with the incident light. Alternating nodes of high and low exposure result, separated at $\frac{\lambda}{4n}$ intervals where n is the refractive index of the resist. The corresponding variations in the inhibitor concentration, M , lead to nonuniform development and result in a steplike

resist profile. By introducing an intermediate layer to match the impedances of the photoresist and the substrate, it is possible to reduce reflections and minimize this effect.

Three easily manufacturable materials are considered for this layer - silicon dioxide, silicon nitride and polysilicon. An existing program, REFLOP¹, is used to determine the optimal thickness for each thin film stack necessary to obtain low reflectivity at the exposure wavelength of 436nm and high reflectivity at the measurement wavelength of 633 nm. The latter property is desired to ensure good zone signals from the DRM.

The values for the reflection coefficient and the standing wave ratio for different thin film stacks are summarized in Table 1. Silicon, on its own, is 24% reflective at 436nm when measured from within the resist, and has a standing wave ratio of 2.8. Addition of 1600 Å of nitride reduces the standing wave ratio to 1.98, a 30% reduction. Best results are obtained using a trilayer of 450 Å of nitride on top of 800 Å of oxide on 1600 Å of nitride. A standing wave ratio of 1.06 is obtained. Actual measurement of the reflectivity of this stack in air using a Perkin Elmer UV/VIS Spectrophotometer is shown in Figure 2.3. Less than 1% reflection is obtained at 436nm. Figure 2.4 compares the DRM results obtained using bare silicon and a matched substrate. The latter gives a more sinusoidal zone signal as well as smoother thickness versus depth curve due to the reduction of standing waves. Sample simulation of resist profile on matched and silicon substrate is shown in Figure 2.5 and confirms the DRM result.

The matched substrate approach can also be applied to characterization in the deep-UV. However, the problem there is aggravated by the high reflectance of silicon at 248nm. REFLOP simulations show that the reflectivity from within the resist is increased from 24% at 436 nm to 58% at 248nm. The minimum reflection that can be achieved using a similar nitride/oxide/nitride stack is 16%. Actual measurements of alternative antireflection coatings in air are given in Table 2. Best results are obtained by coating the wafer with baked photoresist.

3.0 Dissolution Measurements with Metal-ion Free Developers

Matched substrates were coated with ~2 microns of Shipley Microposit 1400-31 photoresist and softbaked at 110 deg C for 50 seconds on a hot plate. The wafers were then exposed on a GCA 6400 wafer stepper at 0.02 second exposure increments. Three commercial developers were studied :- MF312, which is designed for high throughput and MF314 and MF319, which contain surfactants designed for high resolution. The development temperature was controlled at the midpoint of the manufacturer's recommended setting (18 deg C for MF312 CD27 and MF319 developers and 22 deg C for MF314 developer). Previous work by Marriot² has shown that these developers are not temperature sensitive. Although different processing modes are recommended by the manufacturer for these different developers (immersion type development for MF312, spray type development for MF314 and spray and puddle type development for MF319), we are limited in the DRM to immersion type development with moderate agitation from the pump circulatory system.

The built-in DRM data analysis package was used to analyze the six different combinations of developer and agitation conditions shown below.

Table 3. Experimental Matrix

| Run | Developer | Development Condition |
|-----|-----------|-----------------------|
| 1 | MF312 | No Agitation |
| 2 | MF312 | Moderate Agitation |
| 3 | MF314 | No Agitation |
| 4 | MF314 | Moderate Agitation |
| 5 | MF319 | No Agitation |
| 6 | MF319 | Moderate Agitation |

3.1 Resist Development³

The effect of the alkalinity of the developer on the development rate is illustrated in Figure 3.1. The results are taken without agitation to minimize the effect of surfactants. For equal exposures, the more alkaline developer develops faster. Thus, MF314, having the highest concentration of 0.31N, develops the fastest, and MF312 (0.27N) develops slightly faster than MF319 (0.24N). Figure 3.2 shows the improvement in the dissolution rate for each case when moderate agitation is introduced in the tank.

3.2 Resist Contrast

Increased agitation also improves contrast. Contrast is related to the resolution, wall angle and linewidth control of a resist. A measure of contrast is given by the value of gamma, γ . Figure 3.3 shows how γ is found from the slope of the linear portion of a normalized thickness versus log exposure plot. With a high contrast resist/developer system, areas receiving less than the threshold dose will not develop, resulting in vertical resist profiles.

Figures 3.4 show that contrast generally improves with agitation and increased development time. Although both MF314 and 319 contain surfactants, only MF314 show a pronounced improvement with agitation. Figure 3.5 shows that very high contrast ($\gamma > 19$) is obtained after 20 seconds of development in MF314 with agitation. No resist loss is evident in the unexposed region indicating a greater degree of process latitude on the exposure.

Figures 3.6 and 3.7 show the improved contrast of MF319 over MF312 for both agitated and unagitated immersion type development but the effect is not quite as significant as MF314. For both MF312 and 319, resist erosion at lower doses is evident and more tapered profiles can be expected.

4.0 Development Model and SAMPLE Simulations of Profiles

Figure 4.1 is a block diagram for finding rate parameters. Experimental rate (R) data from the DRM is combined with SAMPLE simulation of the exposure state (M) versus depth to obtain plots of R versus M using the program FINDRM⁴. Then a piece-wise linear fit model in the program PARMEX⁴ is used to determine the rate parameters.

The rate model⁵ is shown in Figure 4.2. R_1 , R_2 and R_3 define the bulk development rate. R_1 and R_2 are the limiting rates for fully exposed and unexposed resist, while R_3 is a measure of how fast development rate changes as exposure changes (i.e. the slope of the plot of $\log(\text{rate})$ vs M near $M=1$). Surface retardation effect is accounted for by the higher order parameters and is related to the bulk development rate by multipliers. R_4 is the characteristic retardation depth while R_5 and R_6 are the ratios of the surface rate to the bulk rate at $M=0$ and $M=1$ respectively. R_7 , R_8 , R_9 and R_{10} are needed when a strong dose-dependent surface retardation effect is evident. For this case, two surface functions are fitted over separate M regions.

4.1 Resist Development

A typical rate versus depth for a single exposure zone is shown in Figure 4.3. The development rate is lowest at the surface due to a surface retardation effect⁶ but increases rapidly with depth and saturates to a bulk rate. However, due to attenuation in the resist and adhesion effects, the rate decreases again towards the resist/substrate interface.

Figures 4.4 - 4.6 show the raw data and R parameter curve fit for three commercial developers. The surface retardation effect is more pronounced at lower exposures as evidenced by the wider separation of the two curves at higher M values. Increasing agitation also results in greater surface retardation effects. MF314 in particular shows strong dose dependency with a discontinuity evident at about $M=0.45$ with significantly stronger surface induction effects beyond that value. This may in part account for the very high contrast obtained with MF314.

The corresponding R parameters for the six different combinations of developer and agitation conditions are given in Table 4 and summarize clearly the observations made in Figures 4.4 - 4.6. For all six cases, increasing agitation doubles the value for R_1 . The dose-dependency in surface-rate retardation is also illustrated by R_6 being less than R_5 . The value for R_4 is the largest for MF314 with agitation which agrees with the observation that surface rate retardation is most pronounced there. However, further work is necessary to obtain a closer fit for the rate parameters where strong surface retardation is present (Figure 4.5).

4.2 SAMPLE Simulation

Sample simulation for the six cases of development are shown in Figures 4.7 - 4.9 using all six rate parameters (for full characterization) and using three parameters (for the bulk rate only). A one-micron line/space pattern is simulated using different exposure doses for the different developers but maintaining a constant 60 sec develop time. On the whole, it appears that the effect of agitation on the resist profile (via development rate) is secondary to the surface retardation effect. However, agitation is important to ensure good zones signals from the DRM.

In all cases, surface retardation reduces top loss on the resist line. This gives a lip appearance to the resist profile compared to the profile generated using the bulk rate only. Where its effect is more severe (as in the case of MF314 with agitation), an undercut profile (Figure 4.7a) results. The retardation effect penetrates to a depth of 0.5 microns in the resist as opposed to 0.09 microns for the unagitated case (Figure 4.7b). This effect creates the false impression that the development rate actually increases without agitation.

MF312 shows very little surface retardation. As a result, there is considerable top loss on the resist line in Figure 4.8. For the unagitated case, there is no difference between the two profiles generated using six or three parameters with both cases resulting in resist loss as great as 0.3 microns for a 1.5 micron thick resist.

Similar results are obtained with MF319 although there is less resist erosion than for MF312. However, a higher exposure dose is required to develop a 1 micron space in 60 seconds due to the lower alkalinity of MF319. The dose requirement for each developer is summarized in Table 5.

5.0 Exploration of Surfactant Effects

Surfactants are widely used in industry because they provide better wetting, emulsifying and dispersing properties than can be obtained without their presence. In the IC industry, surfactants are used as wetting agents for etch and development processes to improve uniformity and selectivity. The micelle structure of surfactants result in a large surface to volume ratio and thus provide greater area for reaction. Only very minute quantities (on the order of parts per million) are necessary for these effects. As shown in Figure 5.1, 100 ppm of surfactants in 10% potassium hydroxide can reduce the surface tension from 70 to 10 dyne/cm².

In order to increase our understanding of the effect of surfactants on development, generic surfactants are added to a dilute solution of potassium hydroxide and the development characteristics are analyzed on the DRM and using the R vs M software. Various fluorosurfactants from Du Pont are available for this purpose. These surfactants are classified as anionic, cationic, nonionic and amphoteric depending on the charge carried. The solubility, corrosiveness, extent of foaming as well as the stability of different surfactants in alkaline solutions are considered in selecting the surfactant. In the end, a cationic surfactant, FSC, was used for the experiment.

5.1 Experimental Results

It was surprising to discover that Shipley 1400-31 resist exhibited surface retardation effects in potassium hydroxide without the presence of any surfactants. This suggests that some surface inhibition effect may be built into the resist, either by its chemistry or by the heat treatment it received. Figure 5.2 show that there is at least a 10 second delay before dissolution begins for both agitated and unagitated development in KOH when the resist is exposed with less than 71 mJ/cm² of energy. Agitation increases the development rate but does not increase gamma for potassium hydroxide. However, the resist contrast for potassium hydroxide shown in Figure 5.3 is superior to that of MF319 and 312 (Figures 3.6 - 7).

The results for development with 200 and 400 ppm of a cationic surfactant, FSC, are shown in Figures 5.4 and 5.5. Some of the zones on the wafer were obscured by the foaming action of the developer and only zones with good zone signal are analyzed. The surface induction period is significantly increased to about 50 seconds and the contrast becomes comparable to that of MF314. Superposition of the two data sets show that no further enhancements are obtained by increasing the concentration of the surfactant from 200 to 400 ppm.

5.2 Rate Model and SAMPLE Simulation

The resultant R vs M curves for developing Shipley 1400-31 resist in KOH are shown in Figures 5.6 and 5.7. Because of the severe surface retardation observed with FSC in potassium hydroxide solution, only bulk rate parameters can be fitted to the data at this point. These values are tabulated in Table 4. SAMPLE profiles are presented in Figure 5.8 and show comparable results to that using commercial developers.

6.0 Conclusions

The results presented in this paper demonstrate that it is possible to obtain good development data from the DRM through the use of matched substrates to minimize standing waves and sufficient agitation to prevent the dissolution process from being diffusion limited. A trilevel stack of nitride/oxide/nitride is used for these experiments to reduce the reflection to less than 1% at the exposure wavelength of 436nm. Although the same approach can be applied to deep UV lithography, the problem there is aggravated by the high reflectance of silicon at 248nm. Alternative materials with high absorbtivity (like baked Shipley 2400 resist) may be required.

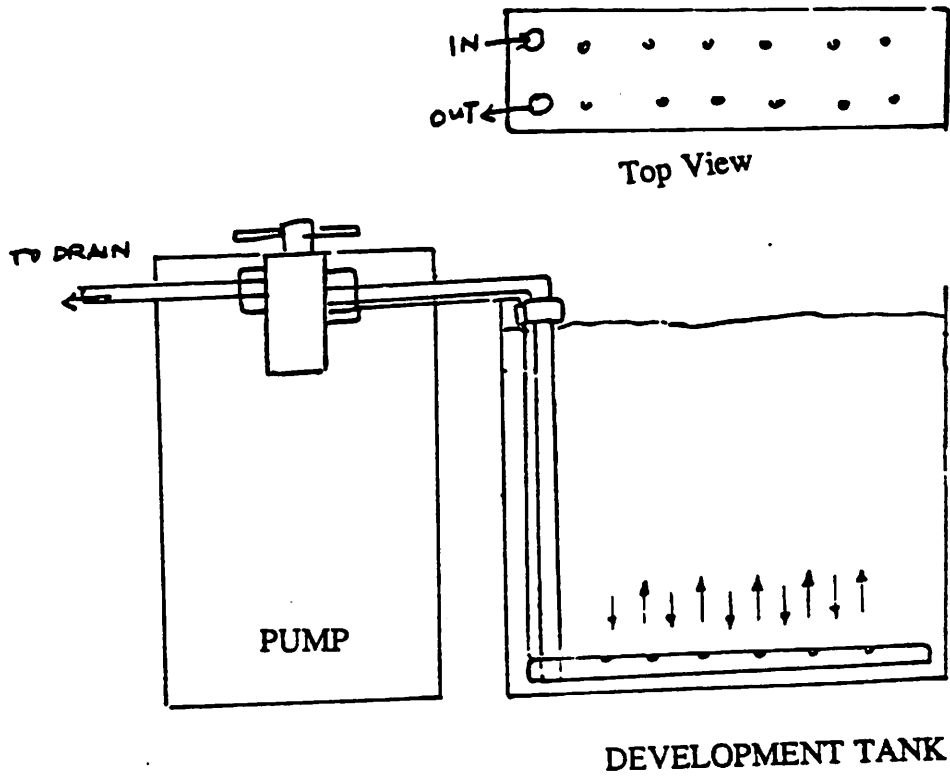
The development characteristics of three commercial metal-ion free developers as well as potassium hydroxide with FSC surfactants were studied as a function of agitation in the development tank. Both developers with surfactants, MF314 and MF319, show improved contrast with agitation although the effect is most pronounced with MF314. It is believed that the improvement in contrast for MF314 is due to enhanced surface retardation by agitating the developer. However, comparable results obtained using potassium hydroxide suggest that part of the surface retardation effect is built into the resist chemistry. Further experiments to study the effect of heat treatment and resist composition as a function of depth are necessary to confirm this point.

The data is analyzed using two new programs, FINDRM and PARMEX. Development rate, R, versus exposure state, M, plots are generated which allow easy identification of surface retardation effects. The rate parameters extracted are used to simulate resist profiles in SAMPLE. All the profiles show rather tapered edges with a protruding lip on the top indicative of surface retardation effects. Of the three developers, MF319 gives the best profile and is also the least sensitive to agitation effects, making it the best choice for manufacturing purposes. MF314 produces a concave profile that may be useful for lift-off applications. However, none of the developers evaluated here give the vertical profile that would have been expected based on the contrast curves from the DRM. This suggests that contrast curves that are commonly used in industry may not be a good measure of the lithographic

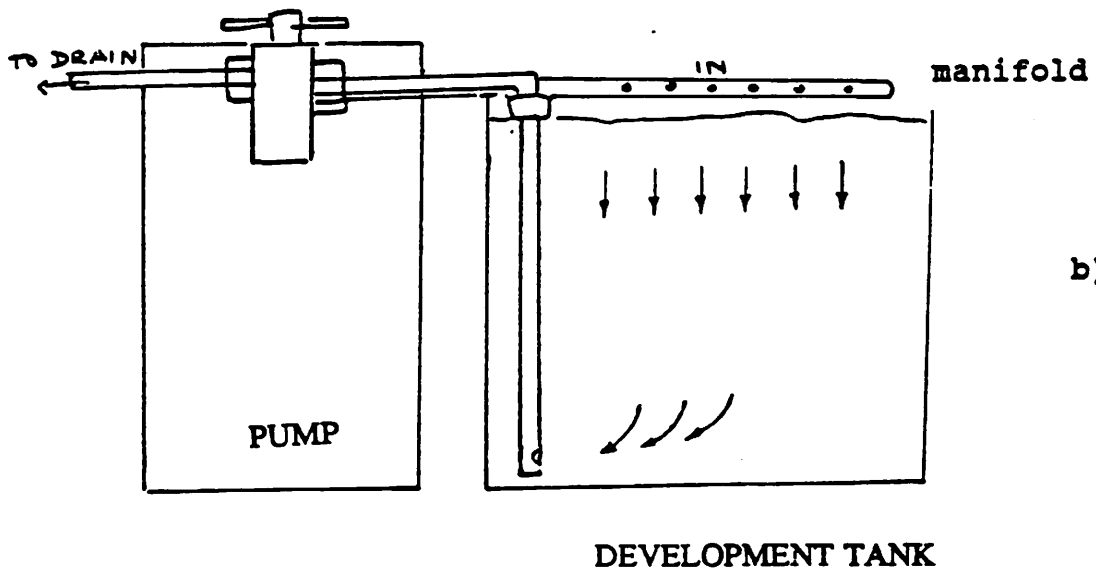
performance of a resist/developer system. R vs M plots and actual profile simulations using extracted rate parameters may be more reliable.

References:

1. REFLOP program, written by W.G. Oldham, University of California, Berkeley.
2. Vic Marriot, "High resolution positive resist developers: A technique for functional evaluation and process optimization," Proceedings of SPIE, vol. 394, p. 144, 1983.
3. W.D. Hinsberg and M.L. Gutierrez, "Effects of Developer Composition on Photoresist Performance," Proc. Kodak Microelectronics Seminar, Interface 83, San Diego, 1983.
4. W.R. Bell II, P. Flanner III, C. Zee, N. Tam, and A.R. Neureuther, "Determination of Quantitative Resist Models from Experiment", submitted to SPIE, Resist V, 1988.
5. D.J. Kim, W.G. Oldham and A.R. Neureuther, "Characterization of Resist Development: Models, Equipment, Method and Experimental Results," Proc. Kodak Microelectronics Seminar, Interface 1982, San Diego, 1983.
6. D.J. Kim, W.G. Oldham and A.R. Neureuther, "Characterization and Modeling of a Resist with Built-in Induction Effect," Proc. Microelectronics Seminar, San Diego, October 1983.

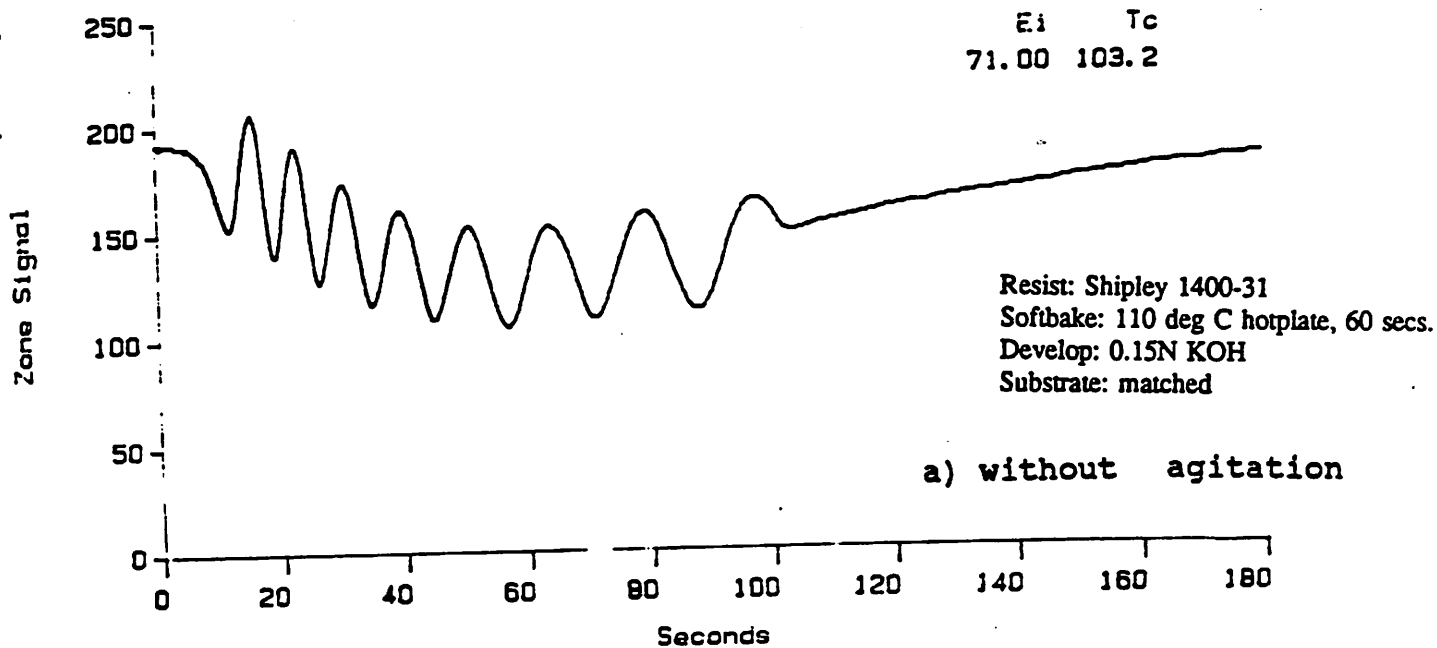


a) Original



b) Improved

Figure 2.1 Circulation Assembly on the DRM



Dreams
V 2.5

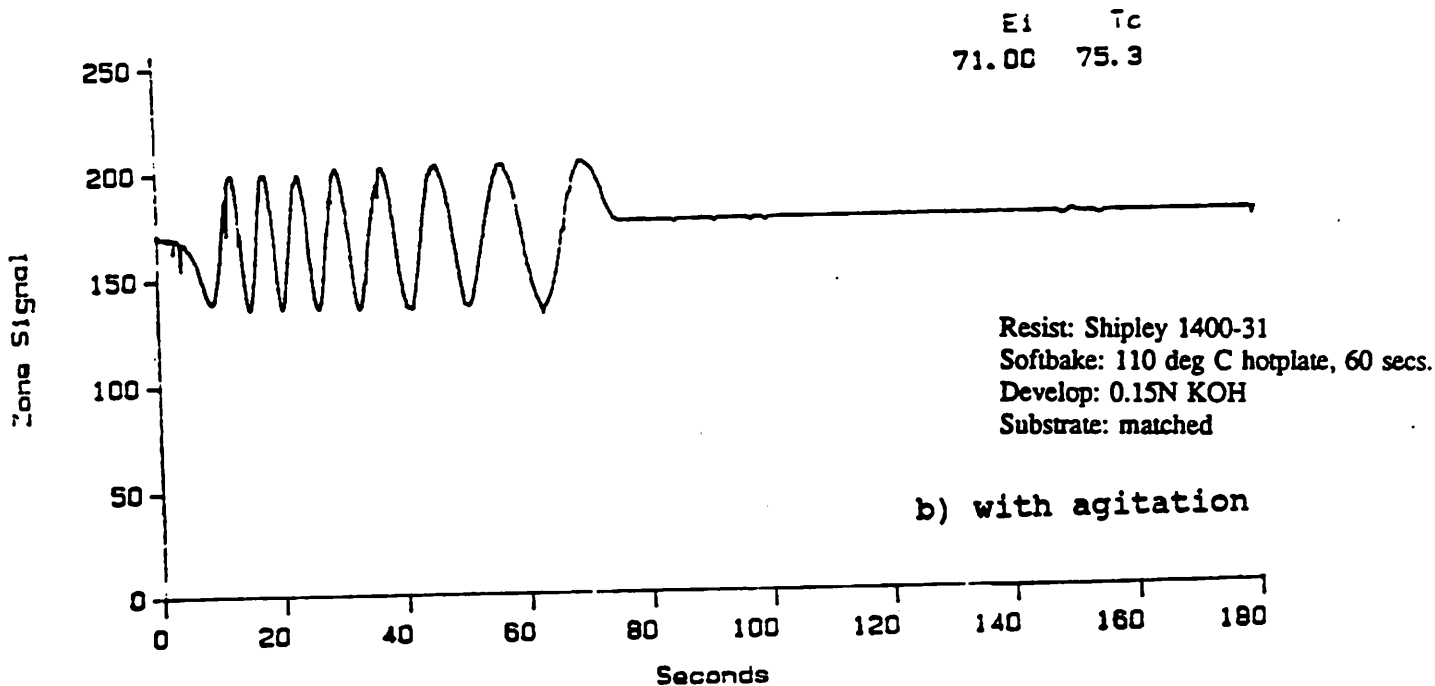


Figure 2.2 Zone signal for 0.15N KOH developer

Table 1. Reflection Coefficient and SWR from within the resist @ 436nm

| Substrate | ρ^2 | ρ | SWR |
|---|----------|--------|------|
| Si | 23% | 0.48 | 2.80 |
| Si/Si ₃ N ₄ | 11% | 0.33 | 1.98 |
| Si/Si ₃ N ₄ /SiO ₂ | 4.8% | 0.22 | 1.56 |
| Si/Si ₃ N ₄ /SiO ₂ /Si ₃ N ₄ | 0.1% | 0.03 | 1.06 |

| |
|--------------------|
| Photoresist n=1.64 |
| Silicon n=4.73 |

| |
|----------------------|
| Photoresist n=1.64 |
| Nitride 450A n=2.02 |
| Oxide 800A n=1.45 |
| Nitride 1600A n=2.02 |
| Silicon n=4.73 |

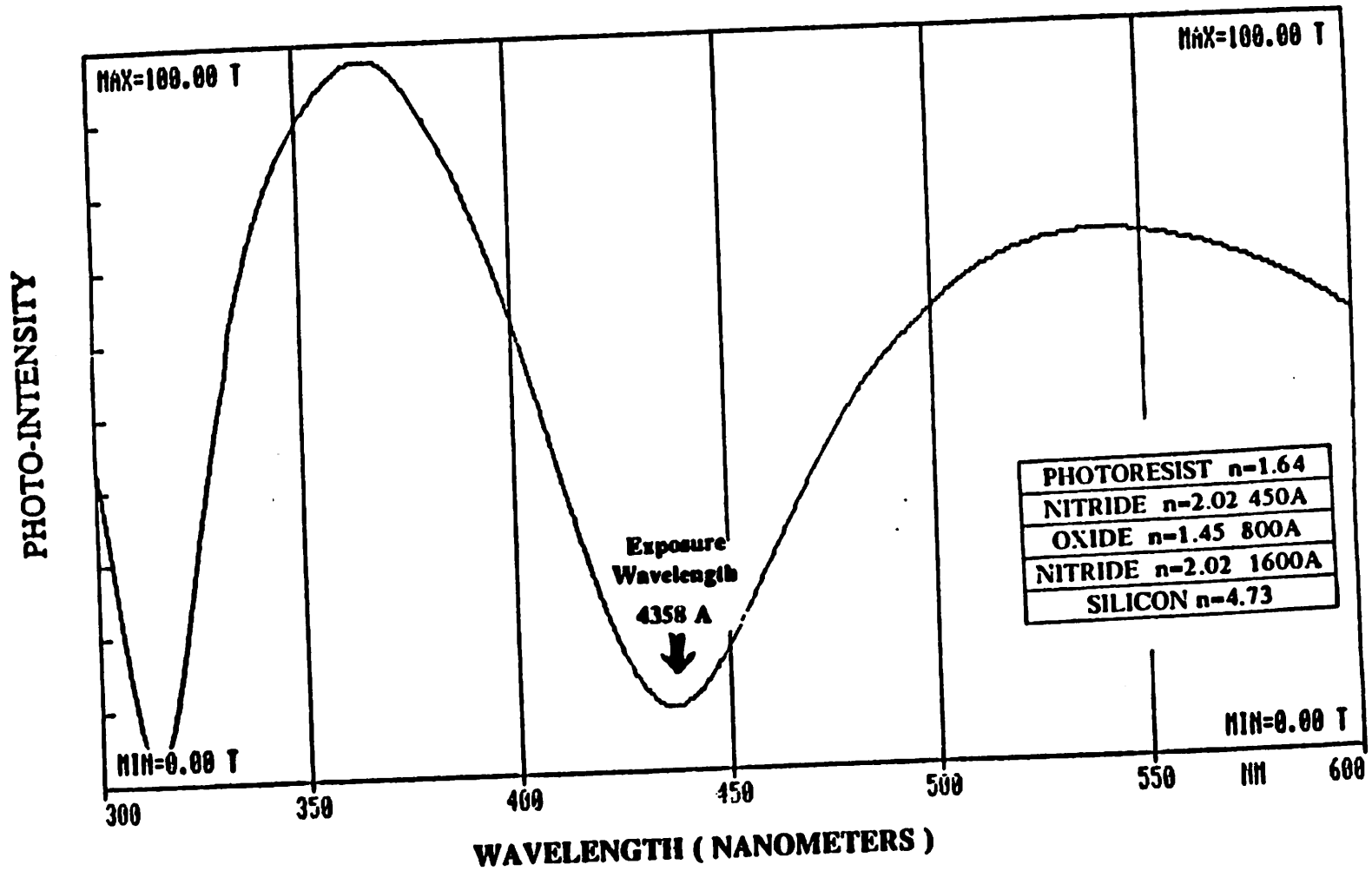


Figure 2.3 Reflectivity of a quasi-matched substrate (measured @ air/silicon interface)

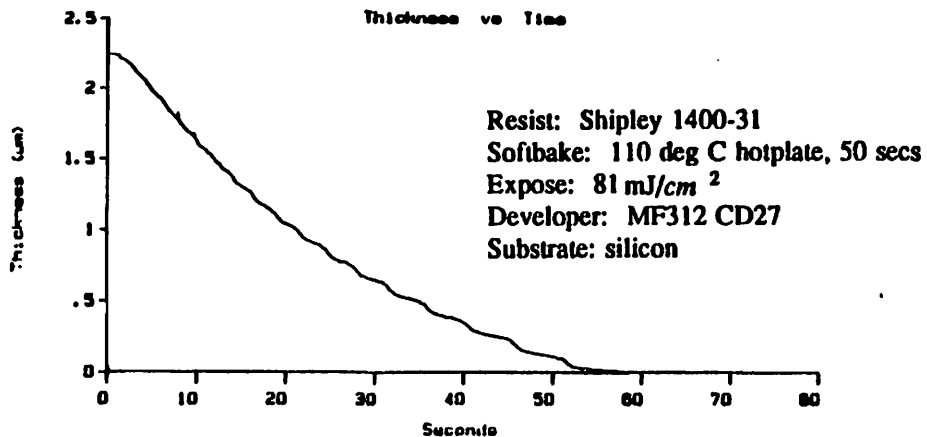
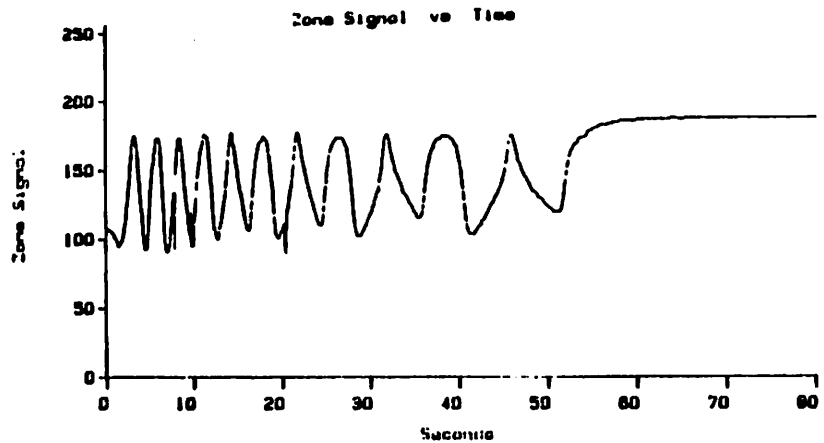
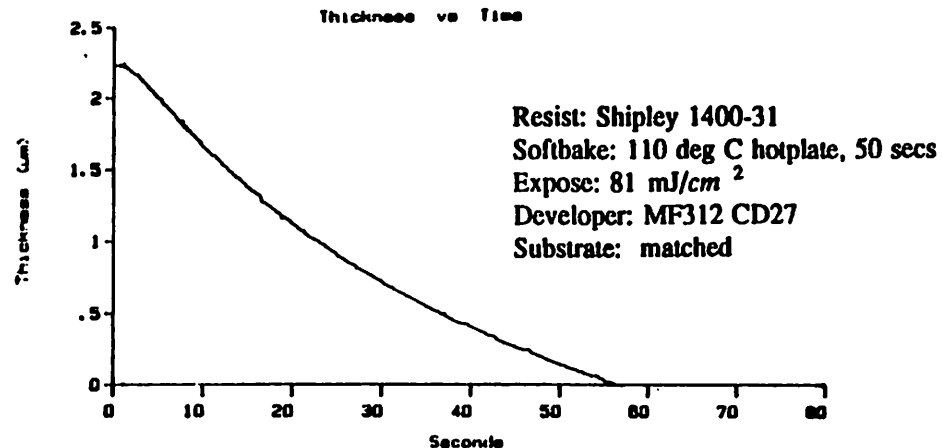
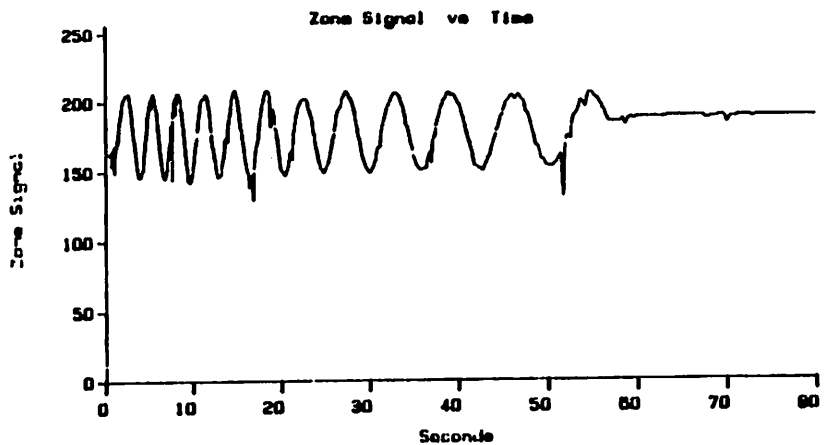


Figure 2.4 Zone signal and thickness vs time curves for matched (top) and silicon (bottom) substrates

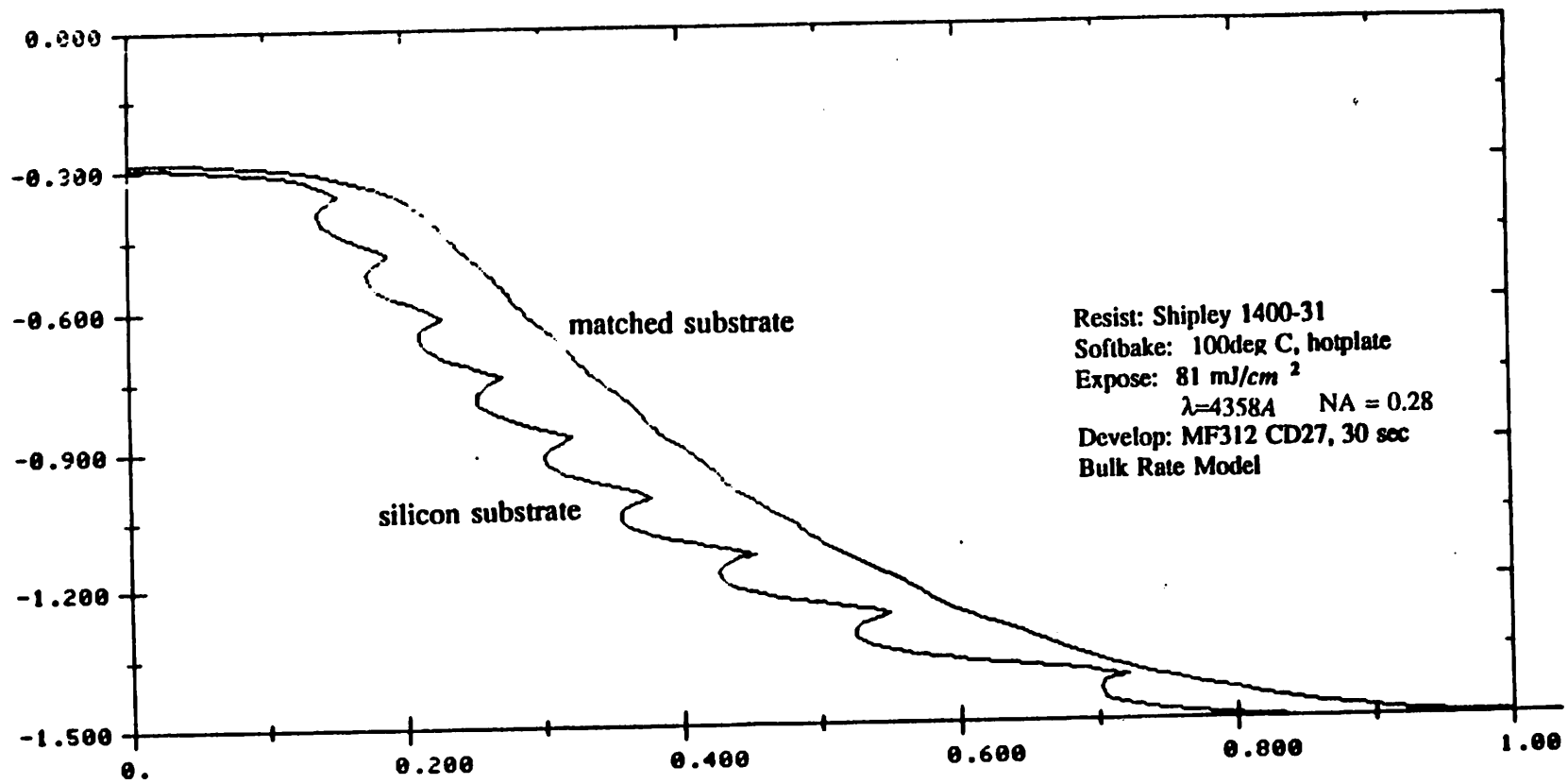


Figure 2.5 SAMPLE simulation of resist profile on matched and silicon substrate

Table 2. Reflection Coefficient and SWR @ 248nm

| Substrate | ρ^2 | ρ | SWR |
|---|----------|--------|------|
| Si (measured in air) | 64% | 0.80 | 9.1 |
| Si (simulated in air) | 72% | 0.85 | 12.3 |
| Si (simulated in PR) | 58% | 0.76 | 7.4 |
| Si/Si ₃ N ₄ /SiO ₂ /Si ₃ N ₄ (simulated in PR) | 16% | 0.39 | 2.3 |
| Si/Al (measured in air) | 83% | 0.91 | 20 |
| Si/baked resist (measured in air) | 7.6% | 0.028 | 1.06 |
| chrome on quartz (measured in air) | 17% | 0.41 | 2.4 |

| |
|------------------------|
| Photoresist n=1.85 |
| Silicon n=1.778-j4.434 |

| |
|------------------------|
| Photoresist n=1.85 |
| Nitride 800A n=2.3 |
| Oxide 425A n=1.54 |
| Nitride 175A n=2.3 |
| Silicon n=1.778-j4.434 |

Dreams

V 2.5

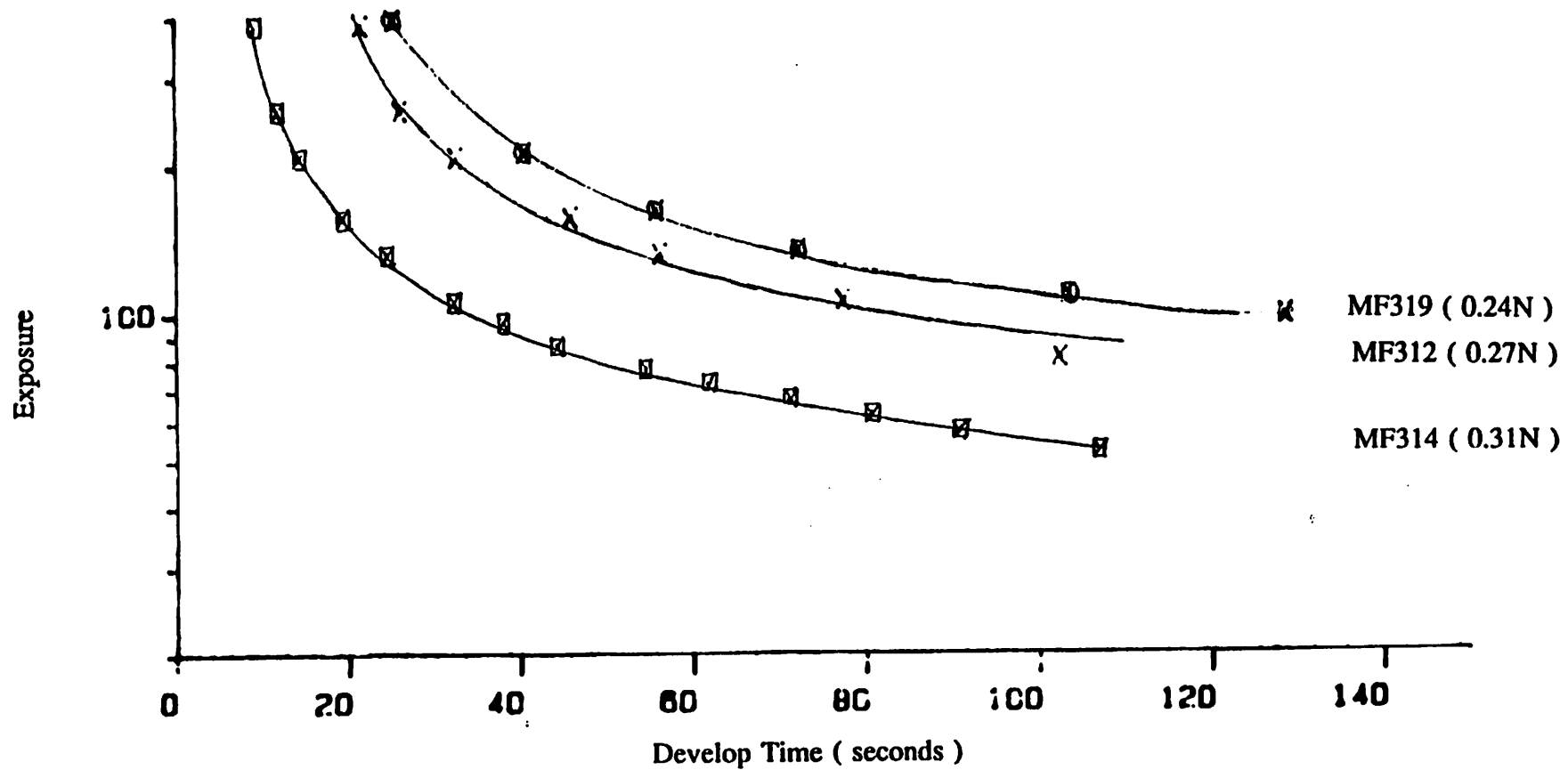


Fig 3.1 Effect of Alkalinity on Development Time

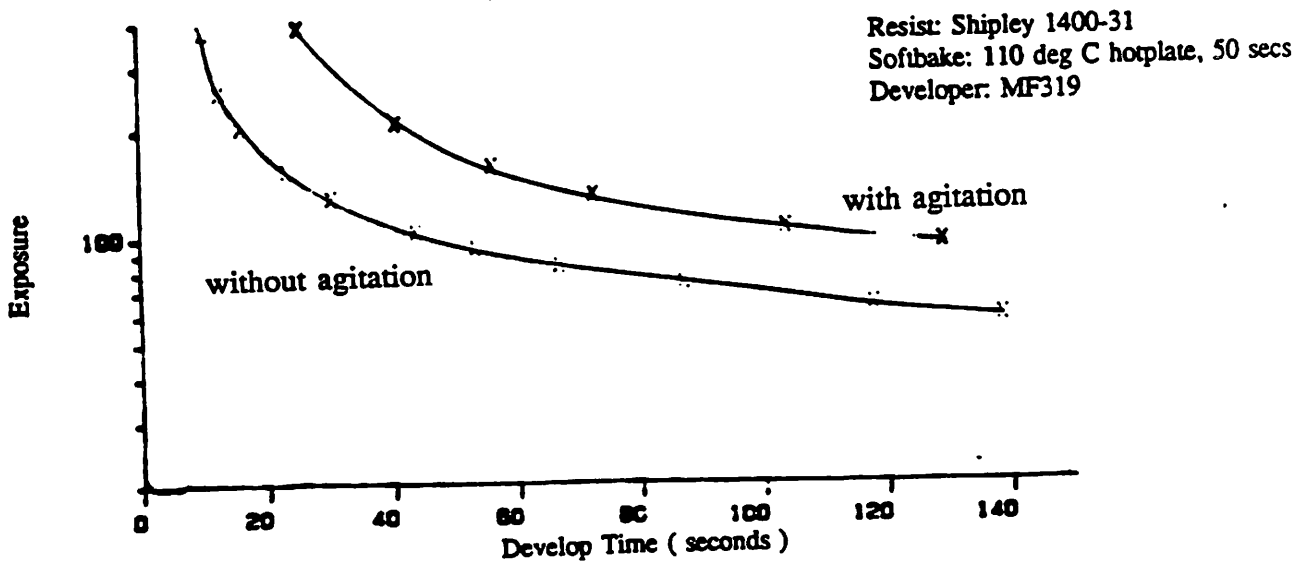
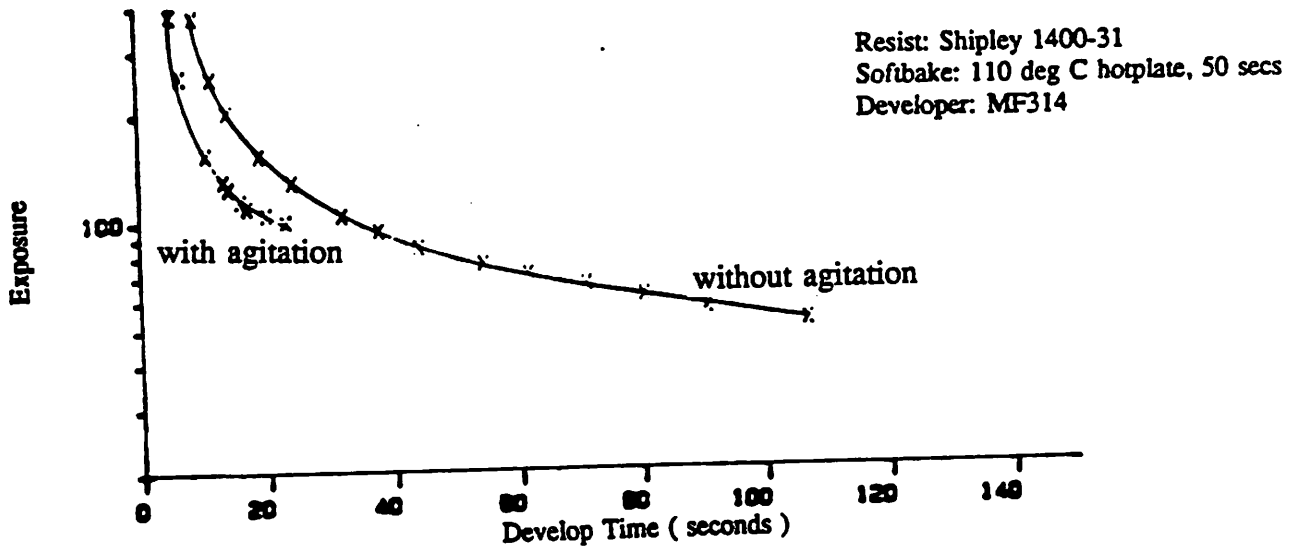
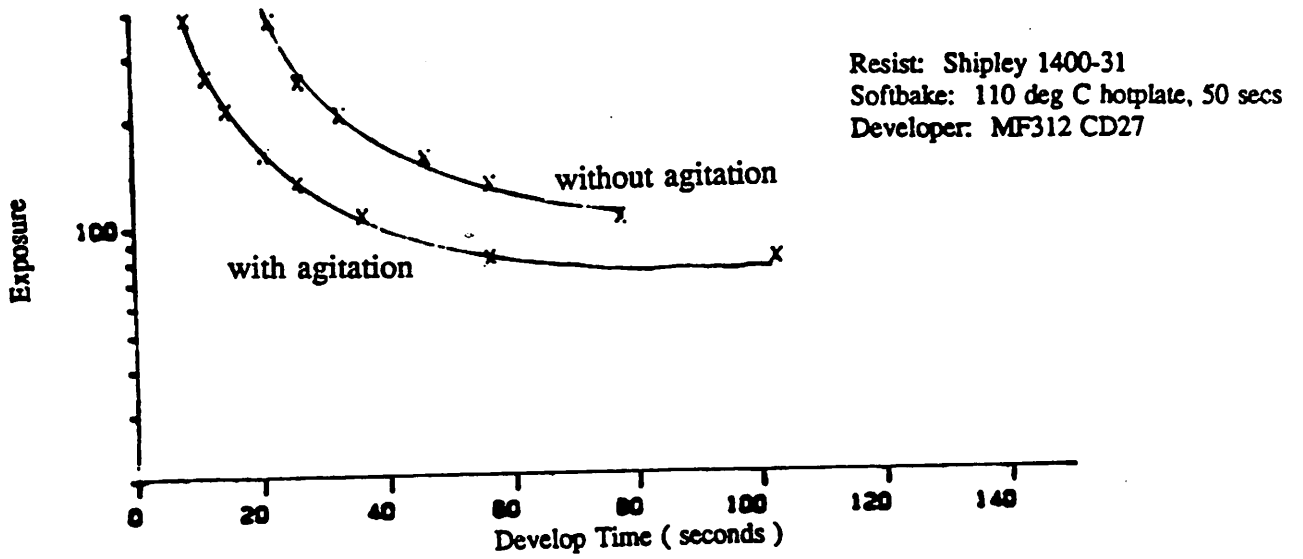


Fig. 3.2 Effect of Agitation on Development Time

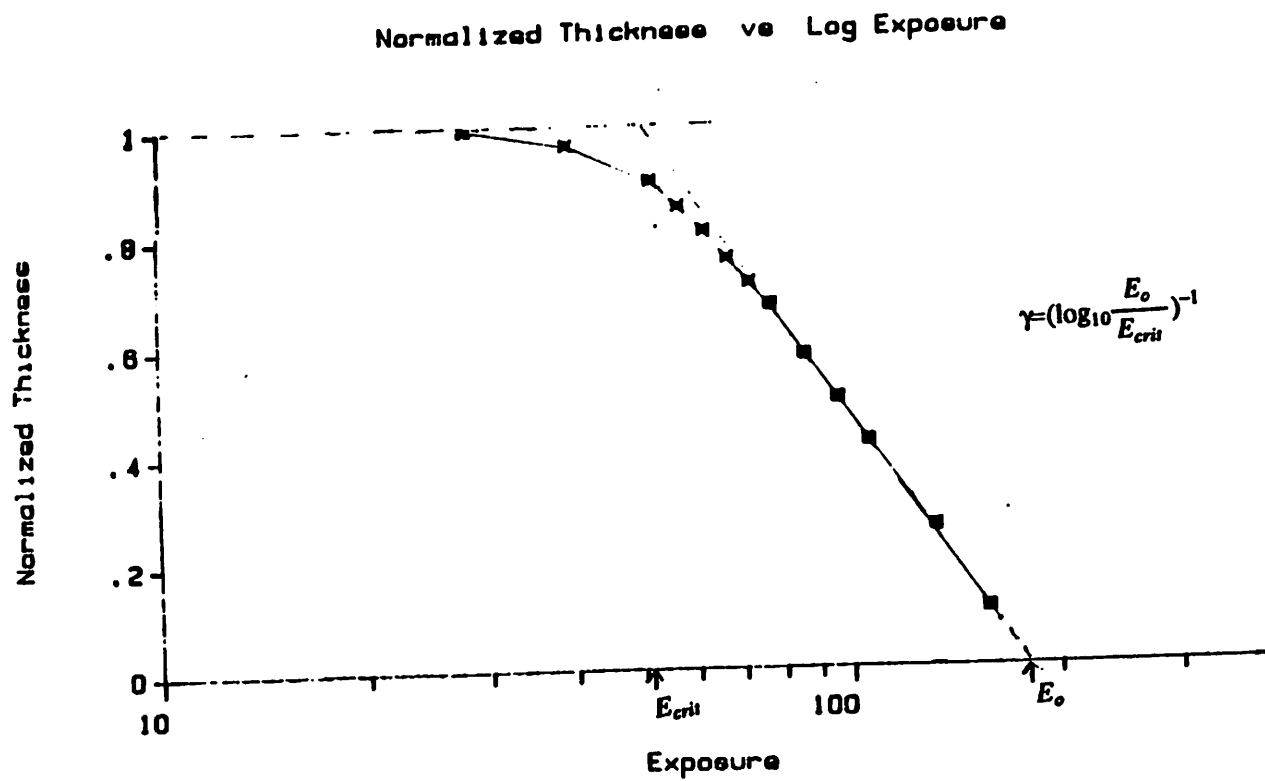


Figure 3.3 Determination of gamma

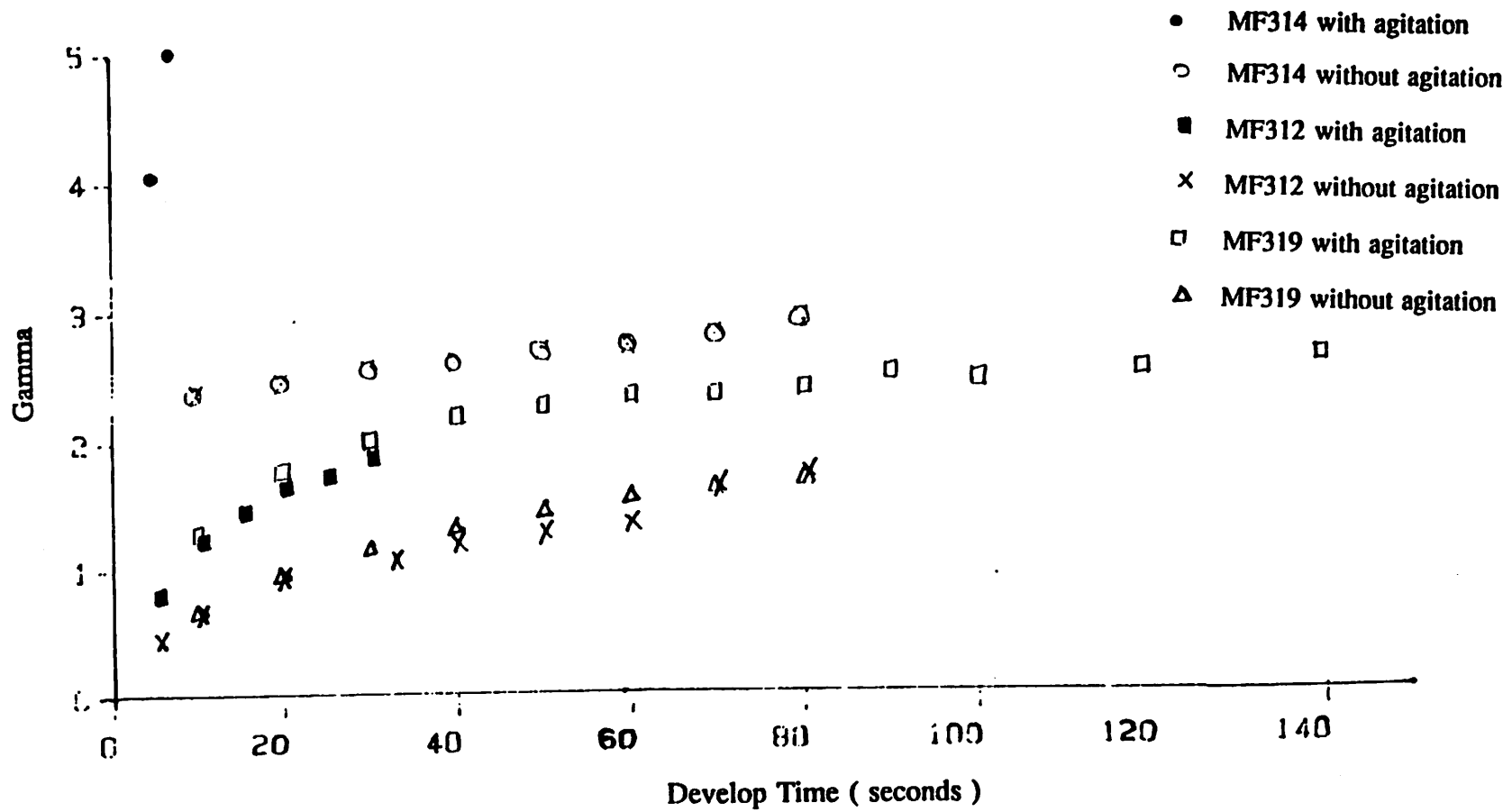
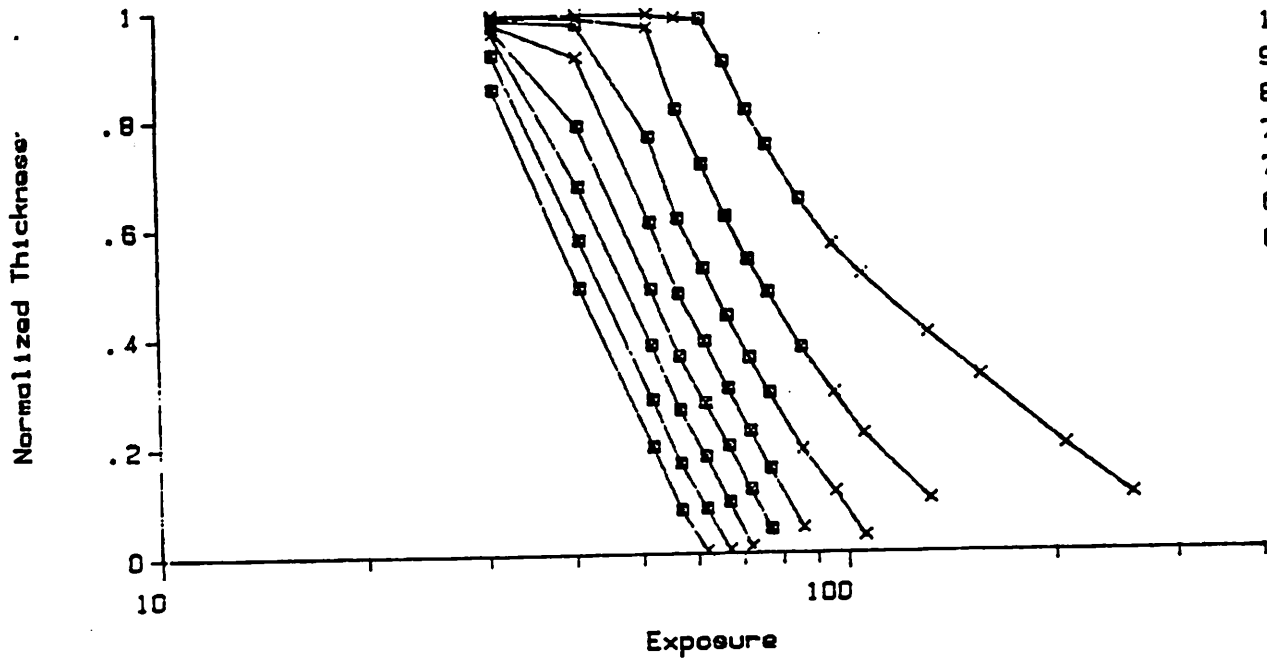


Figure 3.4 Effect of Agitation and Development Time on Gamma

Normalized Thickness vs Log Exposure
 Average Initial Thickness is 1.925 μm

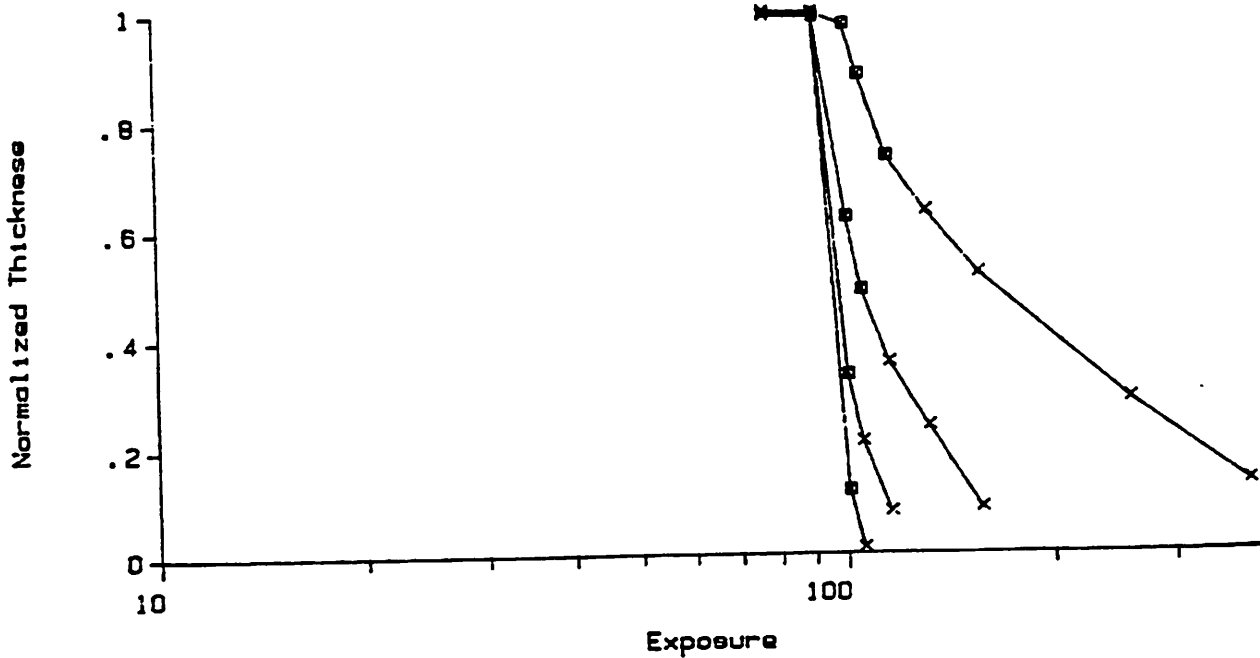


| E_0 | Time |
|-------|------|
| 158.9 | 10.0 |
| 120.1 | 20.0 |
| 99.45 | 30.0 |
| 87.50 | 40.0 |
| 78.93 | 50.0 |
| 71.76 | 60.0 |
| 65.58 | 70.0 |
| 60.45 | 80.0 |

Gamma

| | | | | | | | |
|------|------|------|------|------|------|------|------|
| 2.38 | 2.46 | 2.56 | 2.60 | 2.68 | 2.73 | 2.80 | 2.92 |
|------|------|------|------|------|------|------|------|

Normalized Thickness vs Log Exposure
 Average Initial Thickness is 2.047 μm



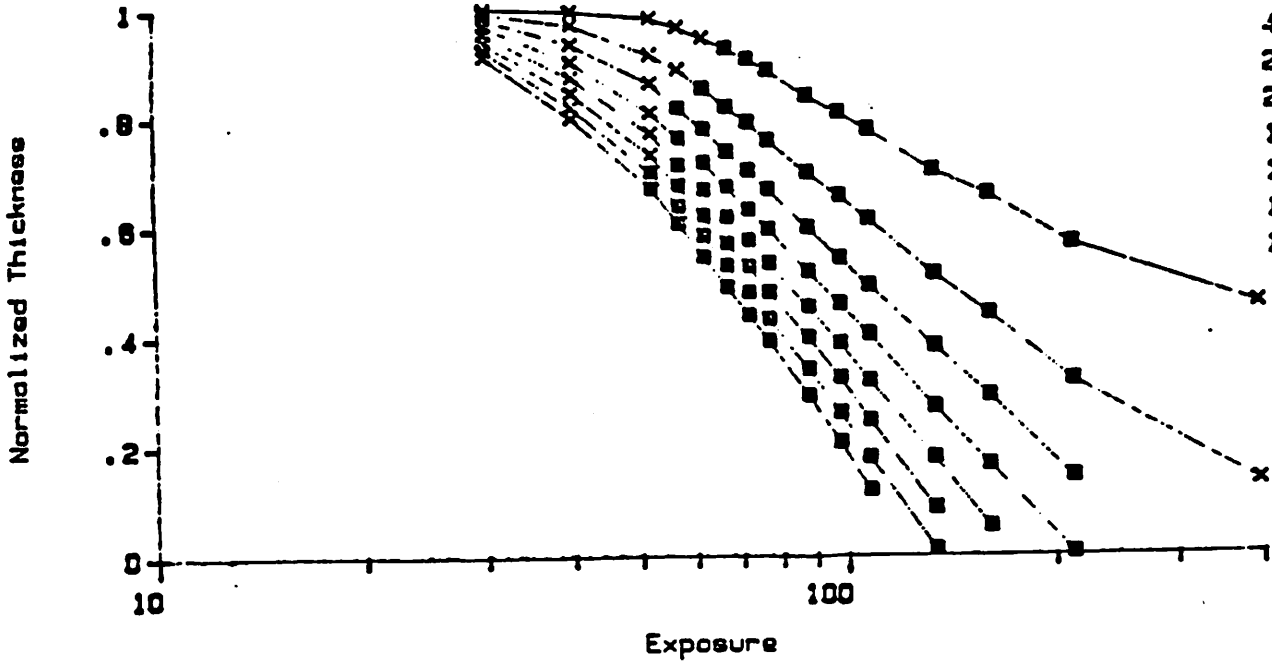
| E_0 | Time |
|-------|------|
| 176.1 | 5.0 |
| 121.9 | 10.0 |
| 106.4 | 15.0 |
| 102.4 | 20.0 |

Gamma

| | | | |
|------|------|-------|-------|
| 4.00 | 7.73 | 14.53 | 19.12 |
|------|------|-------|-------|

Figure 3.5 Contrast Performance of MF314 a) without and b) with Agitation

Normalized Thickness vs Log Exposure
Average Initial Thickness is 1.949 μm

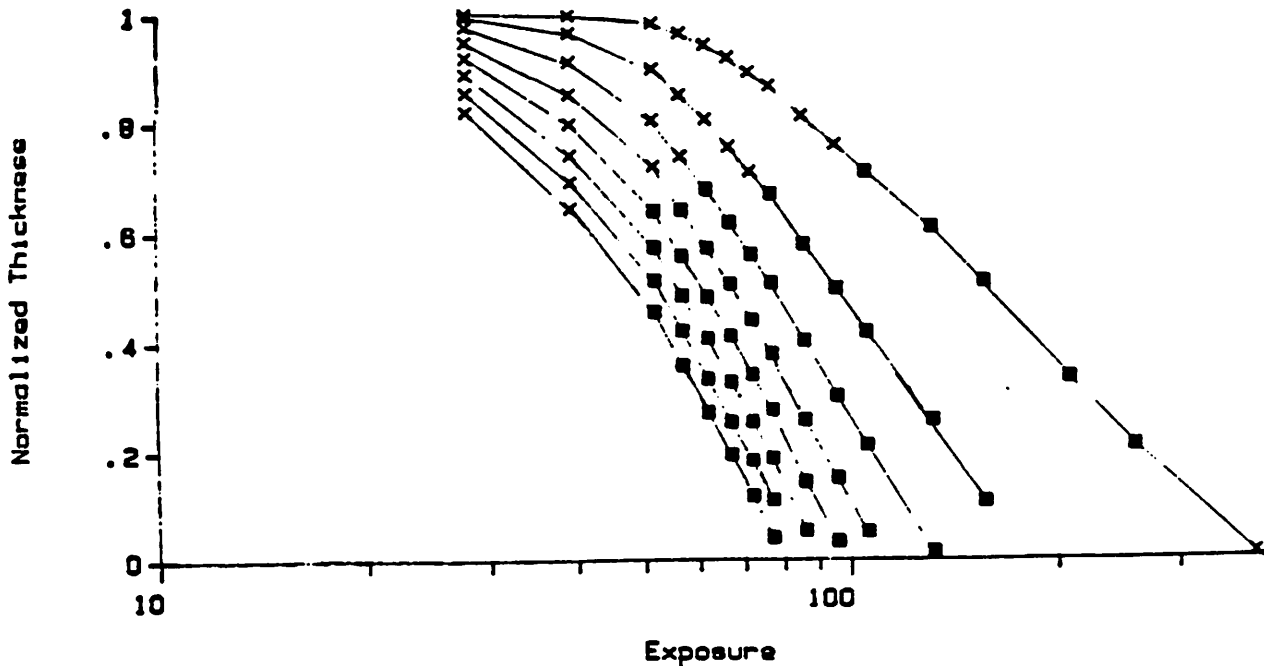


| E_0 | Time |
|-------|------|
| 1267 | 10.0 |
| 436.2 | 20.0 |
| 279.7 | 30.0 |
| 213.5 | 40.0 |
| 178.8 | 50.0 |
| 154.3 | 60.0 |
| 138.1 | 70.0 |
| 126.2 | 80.0 |

Gamma

.72 1.00 1.18 1.33 1.46 1.57 1.66 1.71

Normalized Thickness vs Log Exposure
Average Initial Thickness is 1.938 μm



| E_0 | Time |
|-------|------|
| 375.0 | 10.0 |
| 180.5 | 20.0 |
| 134.3 | 30.0 |
| 112.3 | 40.0 |
| 100.1 | 50.0 |
| 91.63 | 60.0 |
| 85.74 | 70.0 |
| 80.15 | 80.0 |

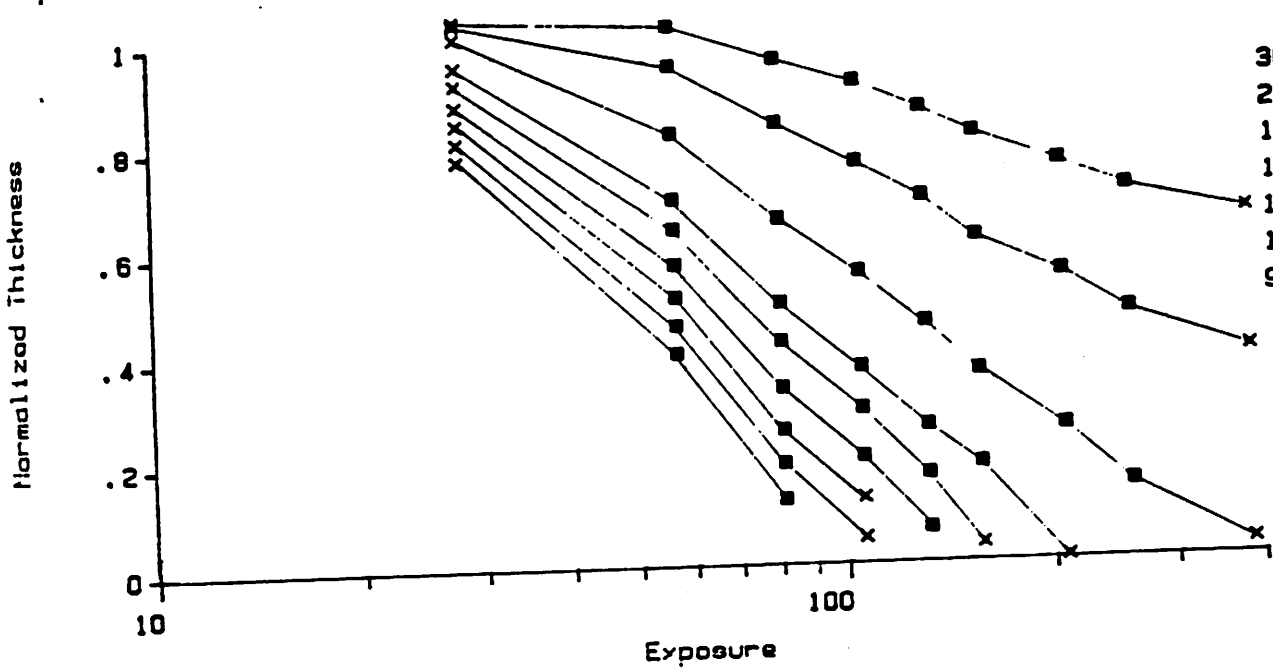
Gamma

1.31 1.80 2.05 2.21 2.28 2.35 2.35 2.41

Figure 3.6 Contrast Performance of MF319 a) without and b) with Agitation

Normalized Thickness vs Log Exposure
Average Initial Thickness is 2.168 μ m

| E_0 | Time |
|-------|------|
| 7120 | 5.0 |
| 1149 | 10.0 |
| 361.3 | 20.0 |
| 221.9 | 32.7 |
| 177.0 | 40.0 |
| 145.7 | 50.0 |
| 114.5 | 60.0 |
| 103.8 | 70.0 |
| 94.00 | 80.0 |

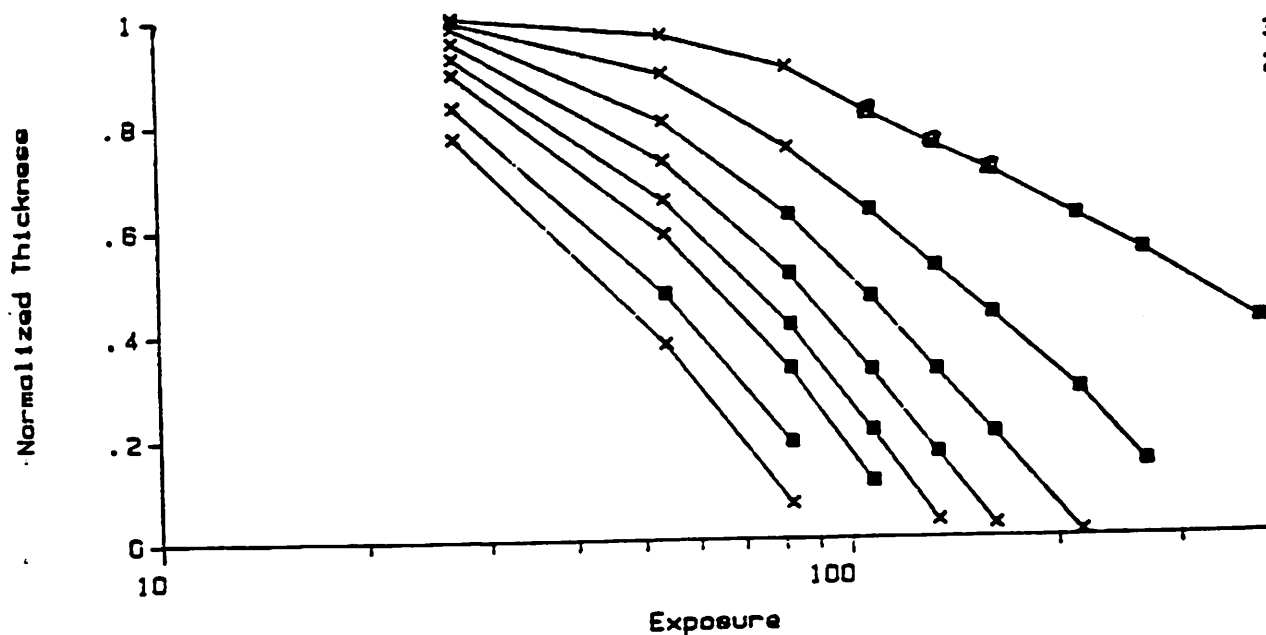


Gamma

| | | | | | | | | |
|-----|-----|-----|------|------|------|------|------|------|
| .47 | .69 | .97 | 1.11 | 1.22 | 1.32 | 1.60 | 1.67 | 1.77 |
|-----|-----|-----|------|------|------|------|------|------|

Normalized Thickness vs Log Exposure
Average Initial Thickness is 2.198 μ m

| E_0 | Time |
|-------|------|
| 1310 | 5.0 |
| 357.6 | 10.0 |
| 224.1 | 15.0 |
| 169.1 | 20.0 |
| 142.4 | 25.0 |
| 123.3 | 30.0 |
| 107.3 | 40.0 |
| - | 50.0 |



Gamma

| | | | | | | | |
|-----|------|------|------|------|------|------|---|
| .78 | 1.22 | 1.43 | 1.62 | 1.70 | 1.83 | 1.57 | - |
|-----|------|------|------|------|------|------|---|

Figure 3.7 Contrast Performance of MF312 a) without and b) with Agitation

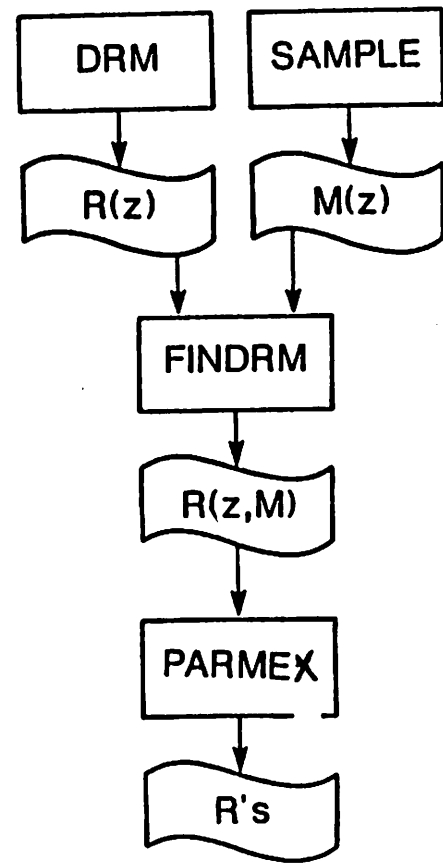
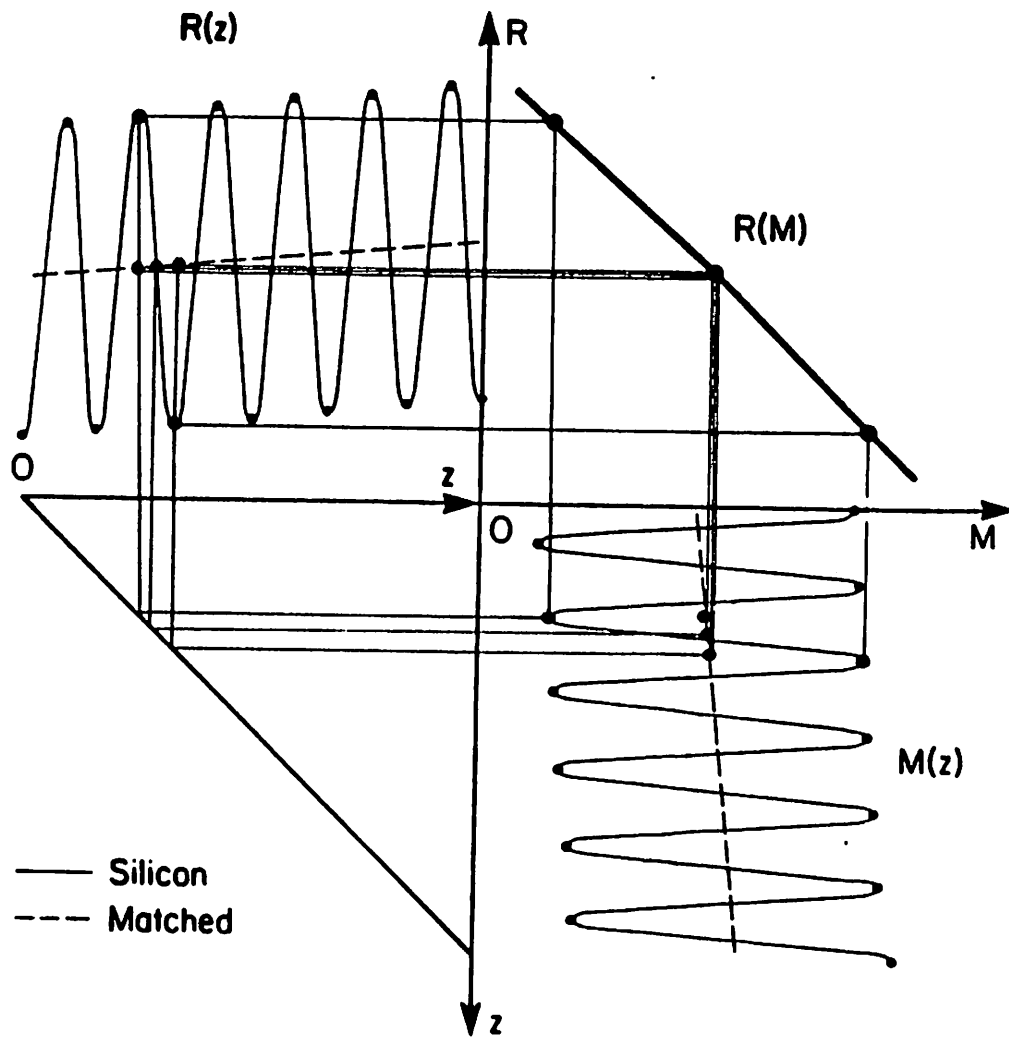
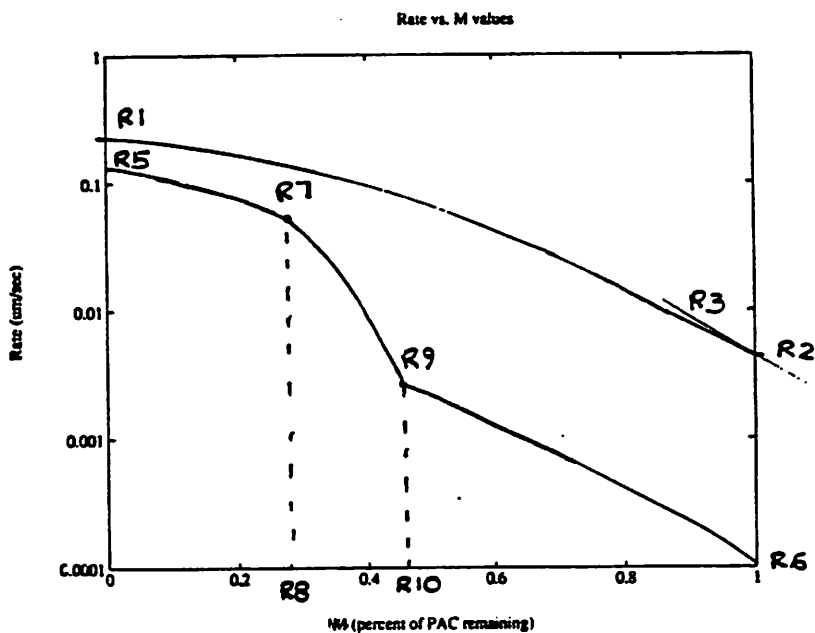


Figure 4.1 Block Diagram

Figure 4.2 Rate Model



Bulk rate

$$R_{bulk} = (R_1^{-1} (1 - M \exp(-R_3(1-M))) + R_2^{-1} M \exp(-R_3(1-M)))^{-1}$$

6 parameter surface retardation model

$$f(z, M) = 1 - (1 - f(0, M)) \exp(-z/R_4)$$

$$f(0, M) = R_5 - (R_5 - R_6)M$$

10 parameter surface retardation model

$$f(0, M) = R_5 + M(R_7 - R_5)/R_8$$

$$0 < M < R_8$$

$$f(0, M) = R_7 + (M - R_8)(R_9 - R_7)/(R_{10} - R_8)$$

$$R_8 < M < R_{10}$$

$$f(0, M) = R_9 + (M - R_{10})(R_9 - R_6)/(R_{10} - 1)$$

$$R_{10} < M < 1$$

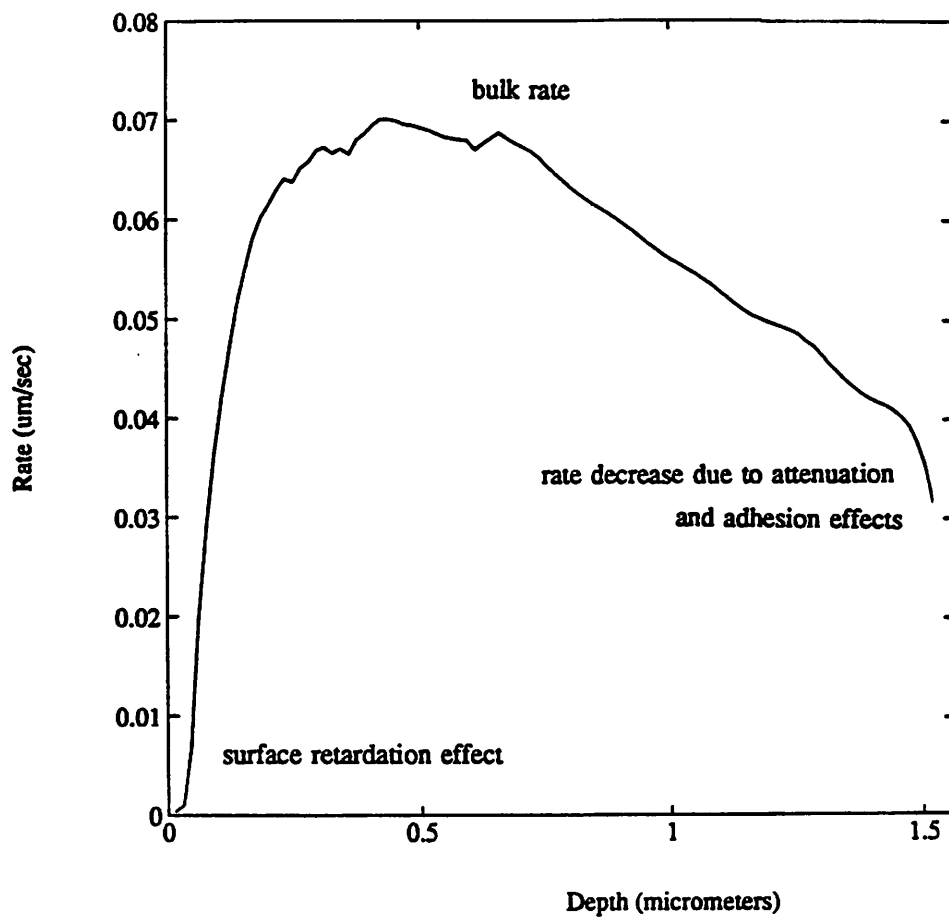


Figure 4.3 Typical plot of development rate versus depth

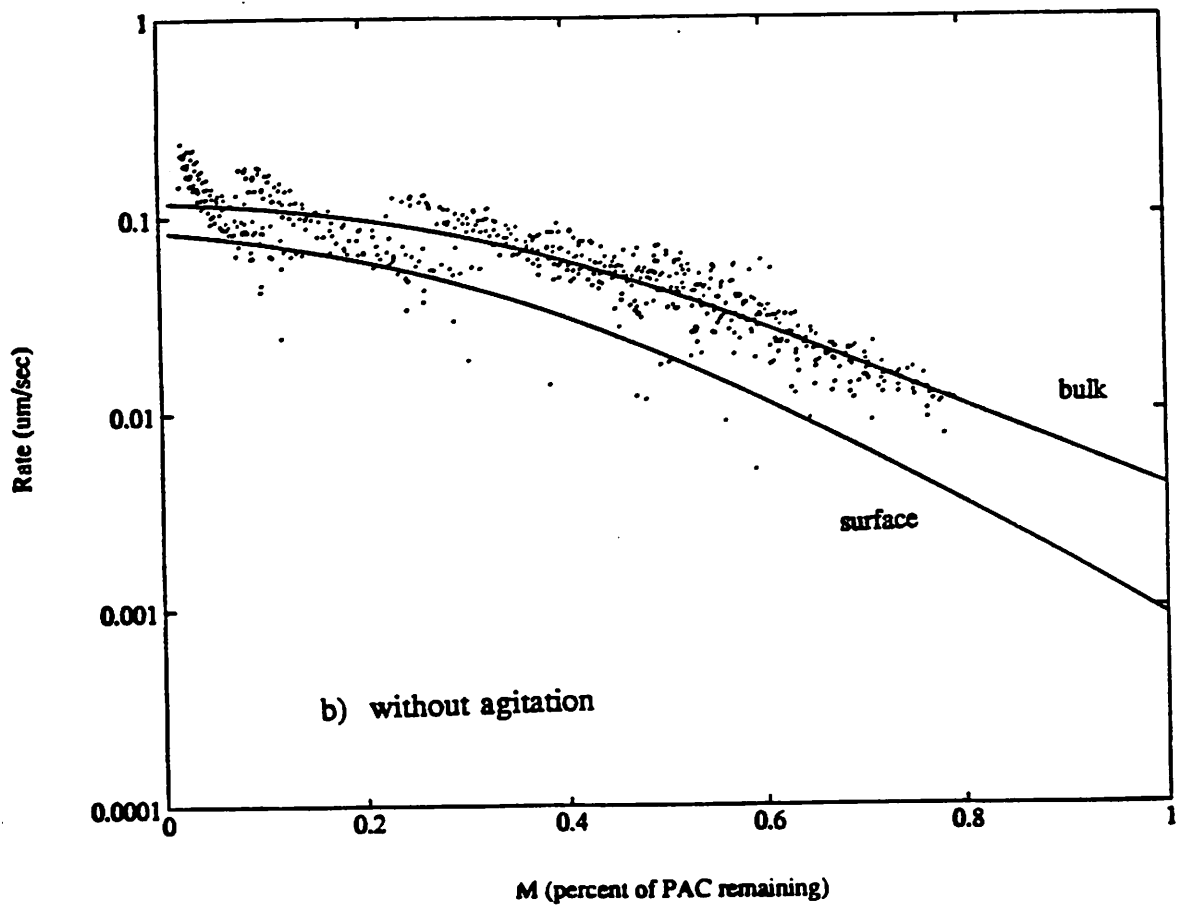
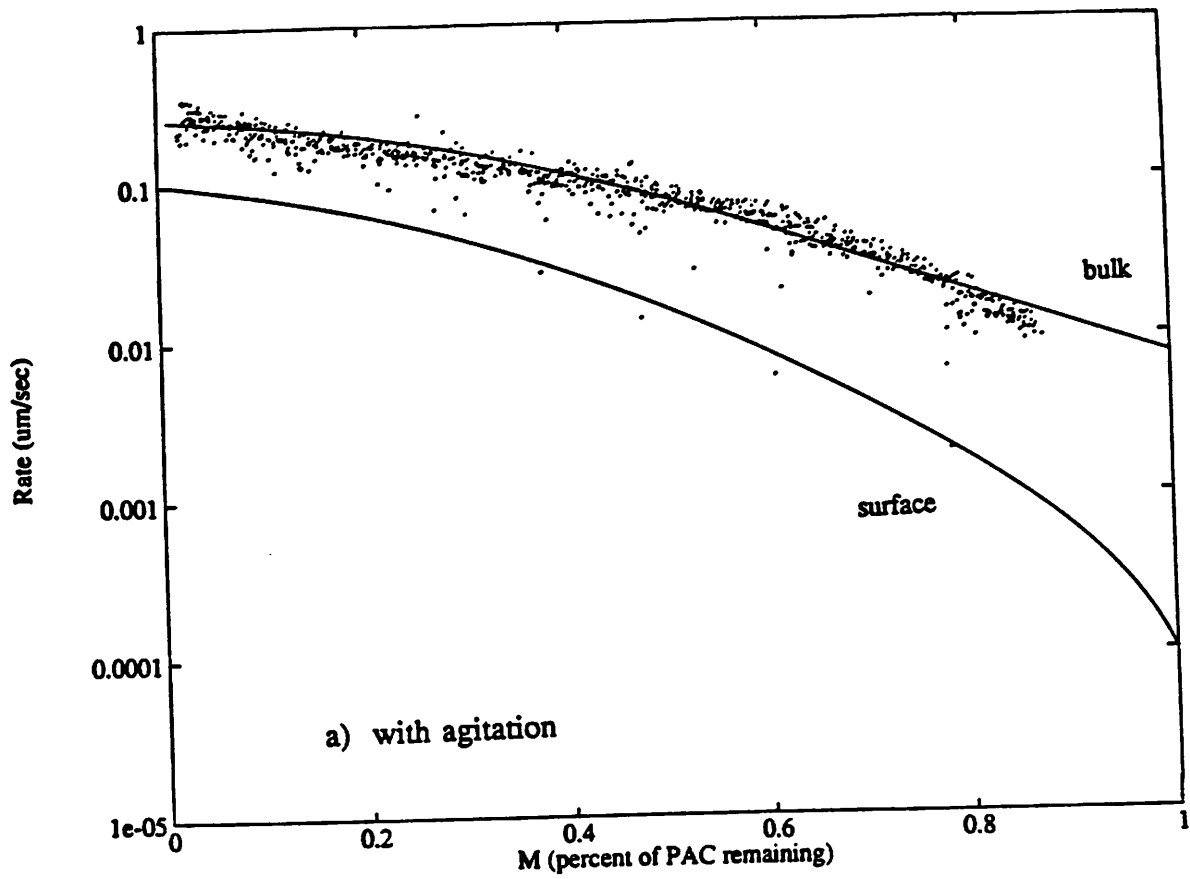


Figure 4.4 R vs M plots for MF312

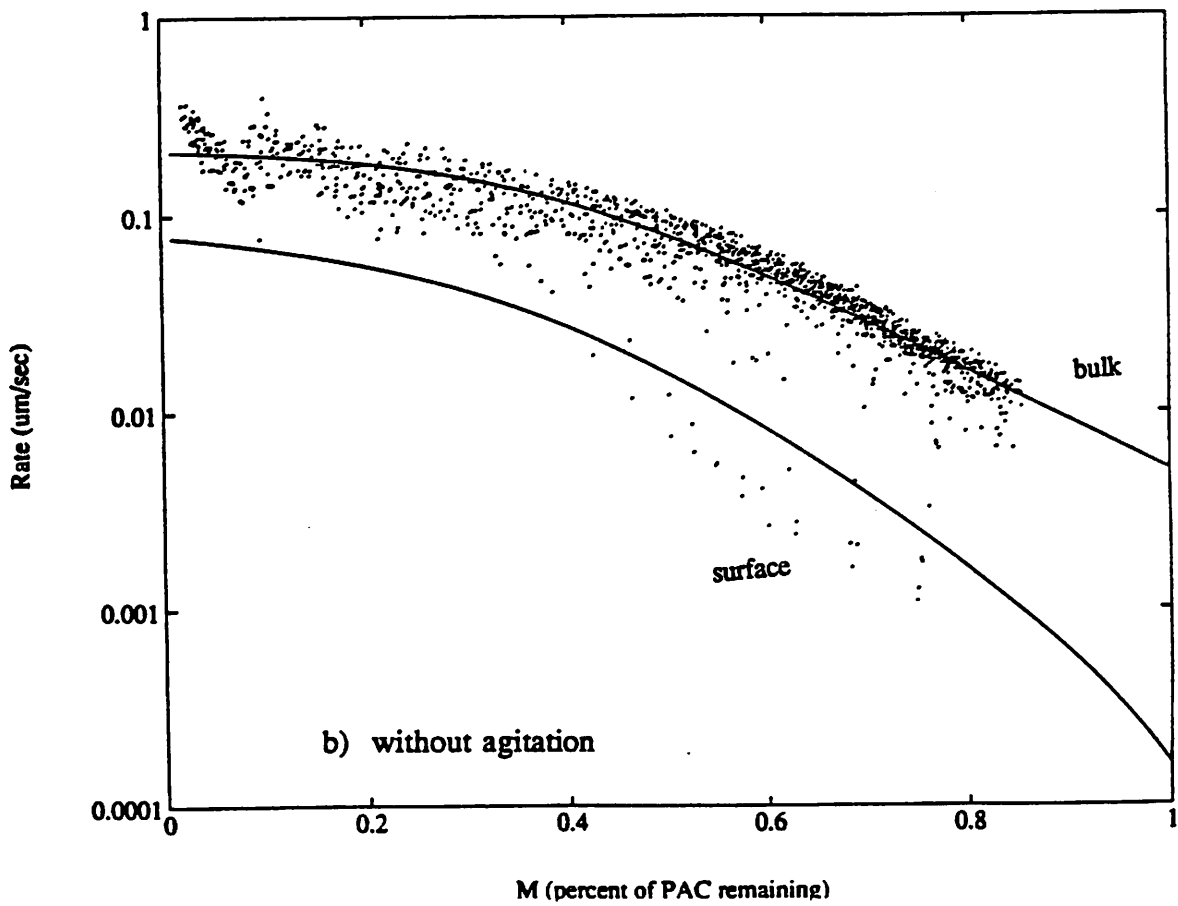
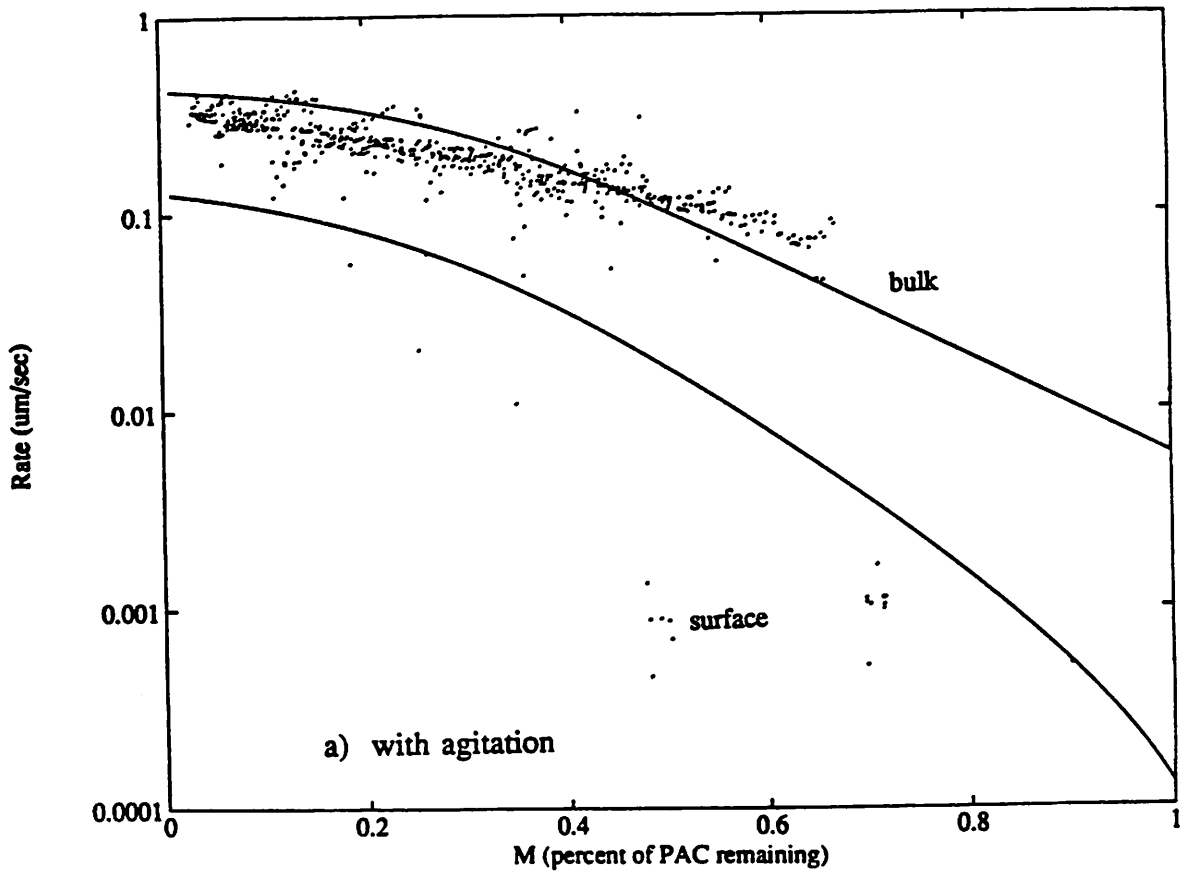


Figure 4.5 R vs M plots for MF314

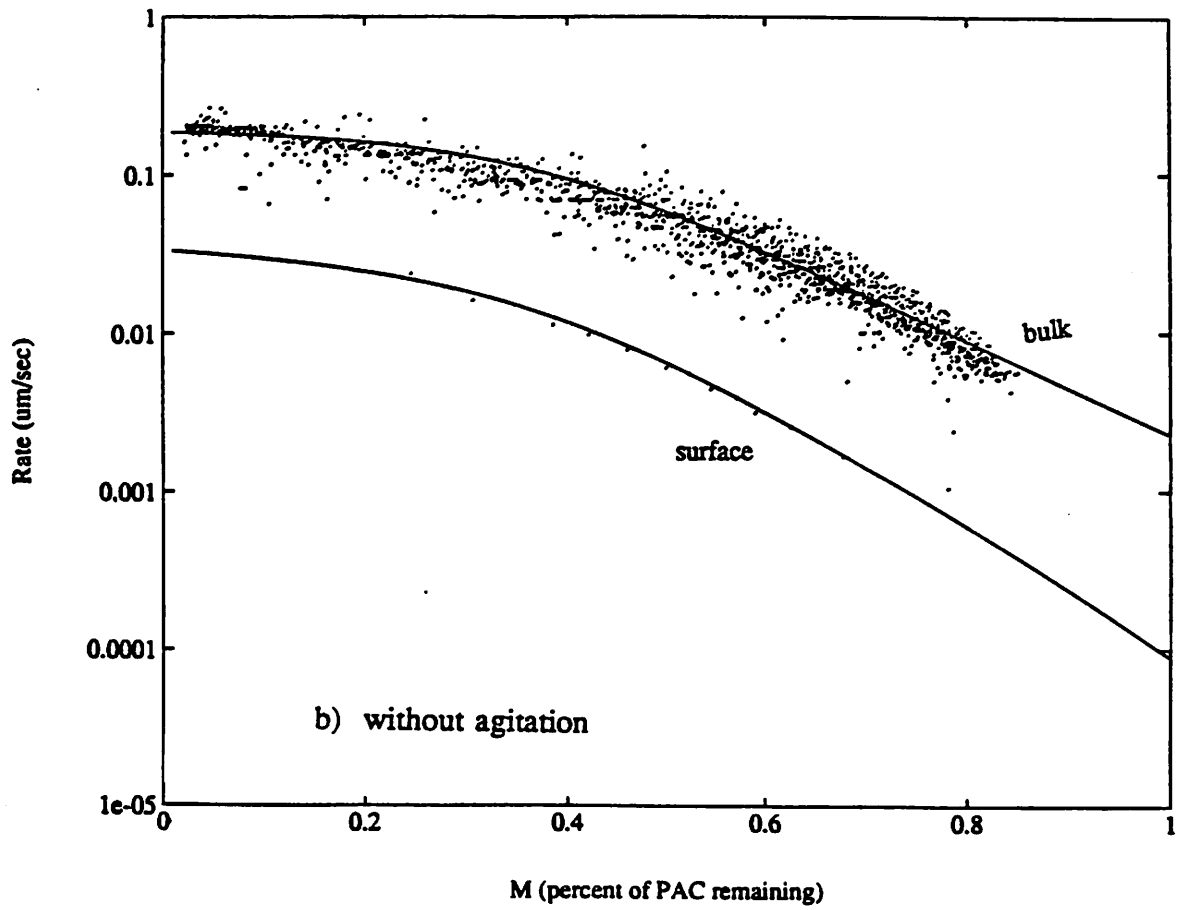
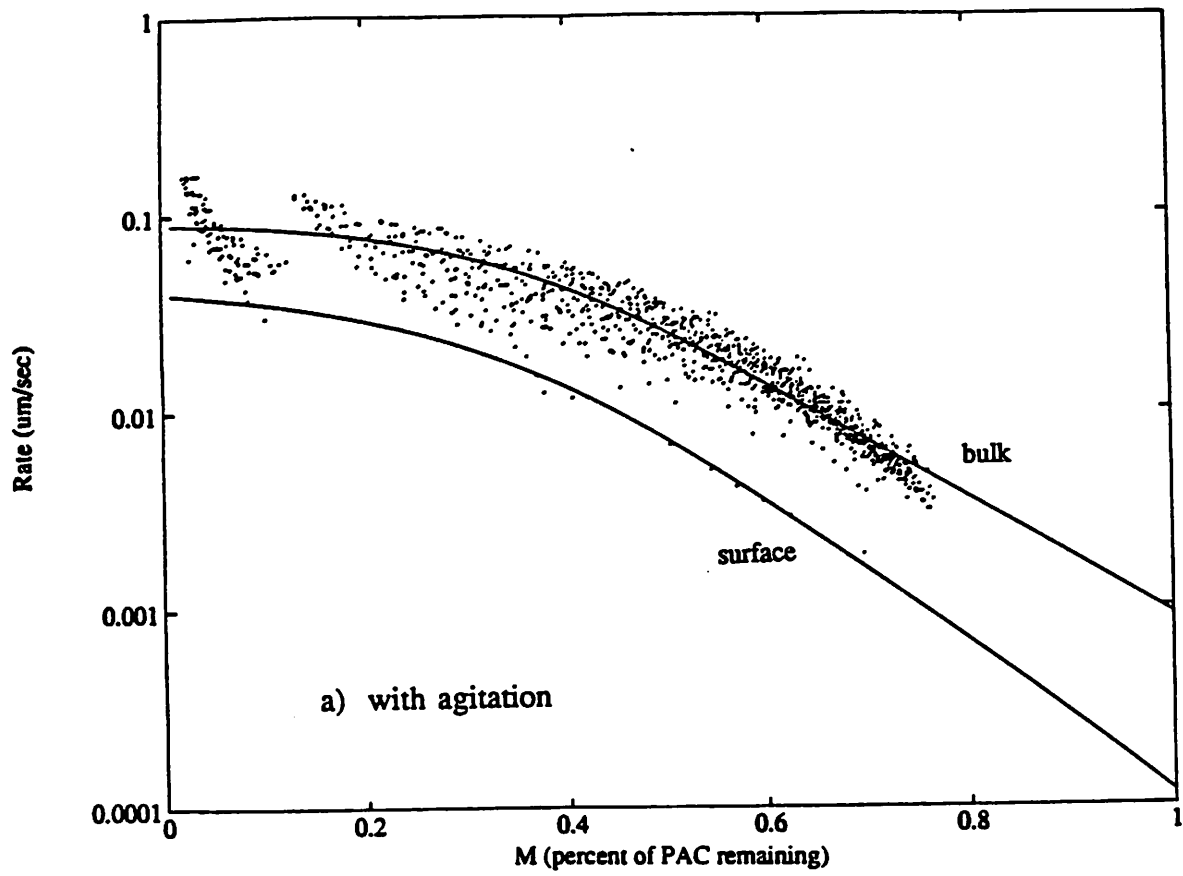


Figure 4.6 R vs M plots for MF319

Table 4. Rate Parameters

| DEVELOPER | R1 ($\mu\text{m}/\text{sec}$) | R2 ($\mu\text{m}/\text{sec}$) | R3 | R4 (μm) | R5 | R6 |
|----------------------|------------------------------------|------------------------------------|-------|-------------------------|--------|----------|
| MF312 w/ Agitation | 0.2431 | 0.007289 | 4.044 | 0.1585 | 0.6393 | 0.07656 |
| MF312 no Agitation | 0.1190 | 0.004116 | 4.019 | 0.03115 | 0.7141 | 0.2202 |
| MF314 no Agitation | 0.2101 | 0.005051 | 5.008 | 0.09489 | 0.371 | 0.03182 |
| MF314 w/ Agitation | 0.4250 | 0.005894 | 4.84 | 0.5037 | 0.3034 | 0.0219 |
| MF319 no Agitation | 0.08959 | 0.0009192 | 5.857 | 0.02478 | 0.4461 | 0.1263 |
| MF319 w/ Agitation | 0.1849 | 0.002271 | 5.841 | 0.1167 | 0.1825 | 0.03865 |
| KOH no Agitation | 0.1356 | 0.001372 | 5.66 | 0.05181 | 0.1254 | 0.006635 |
| KOH w/ Agitation | 0.2763 | 0.00152 | 6.49 | 0.1425 | 0.1004 | 0.01929 |
| KOH w/ FSC Agitation | 0.1138 | 0.002267 | 5.458 | - | - | - |

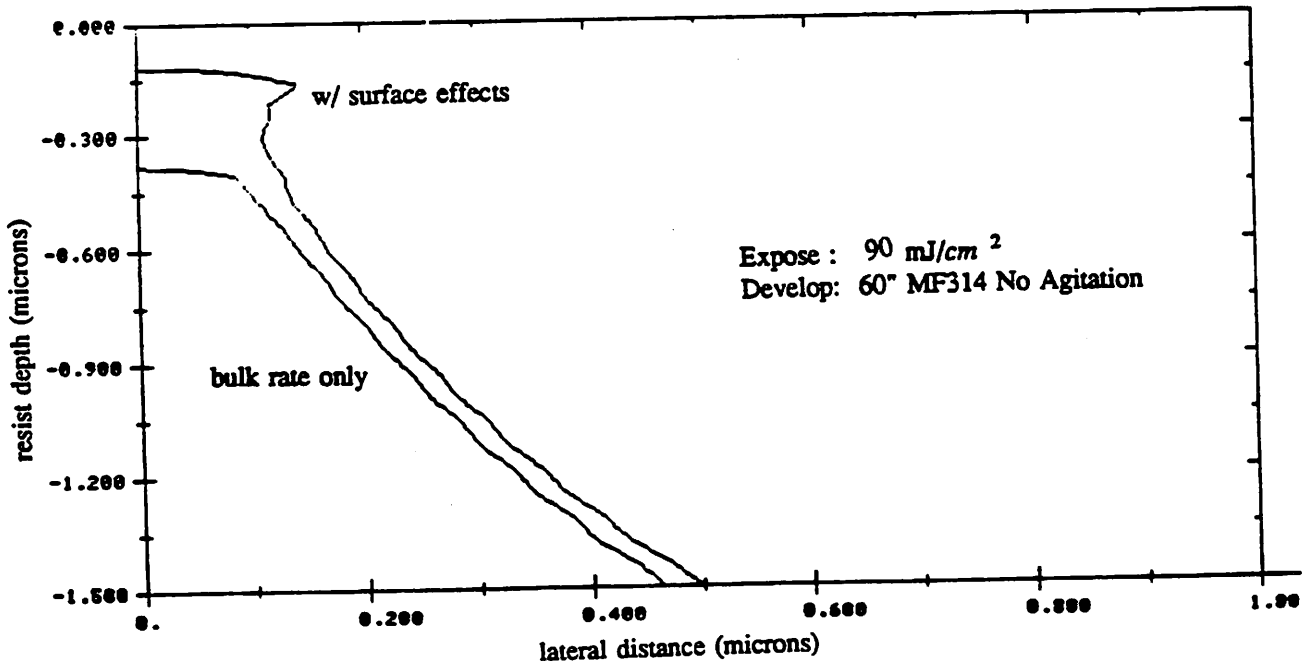
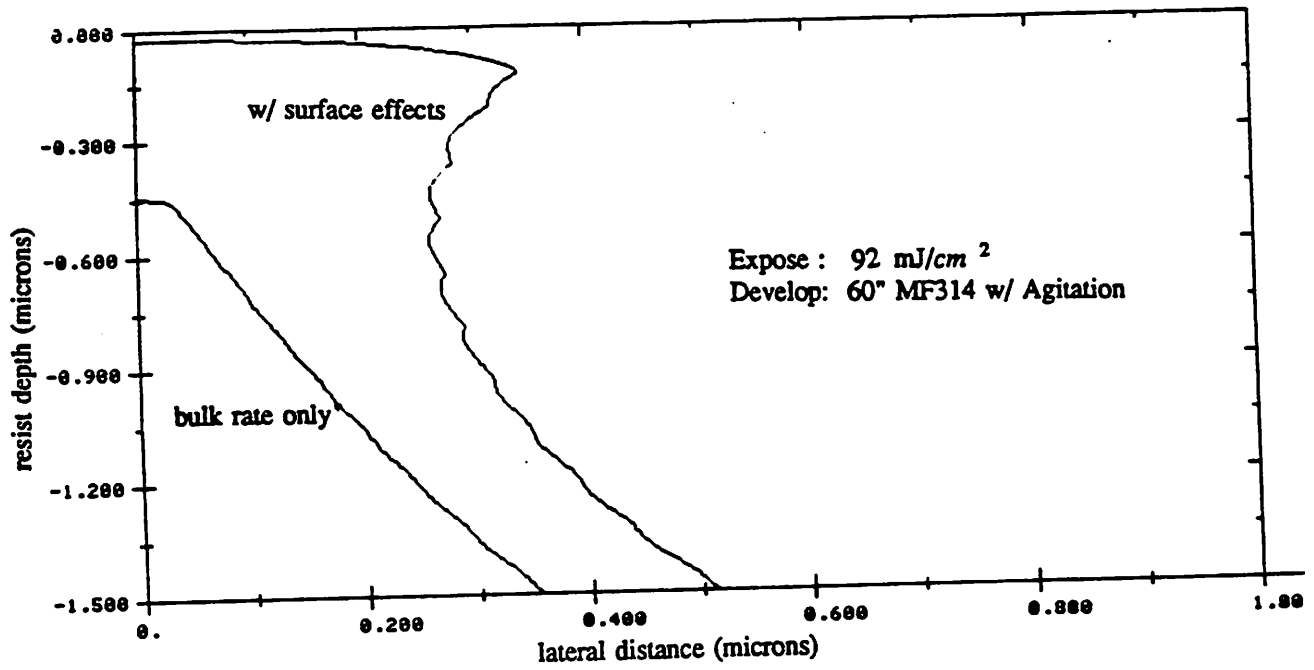


Figure 4.7 SAMPLE profile for MF314 developer using 3 rate parameters (bulk rate) and 6 rate parameters (including surface retardation effects)

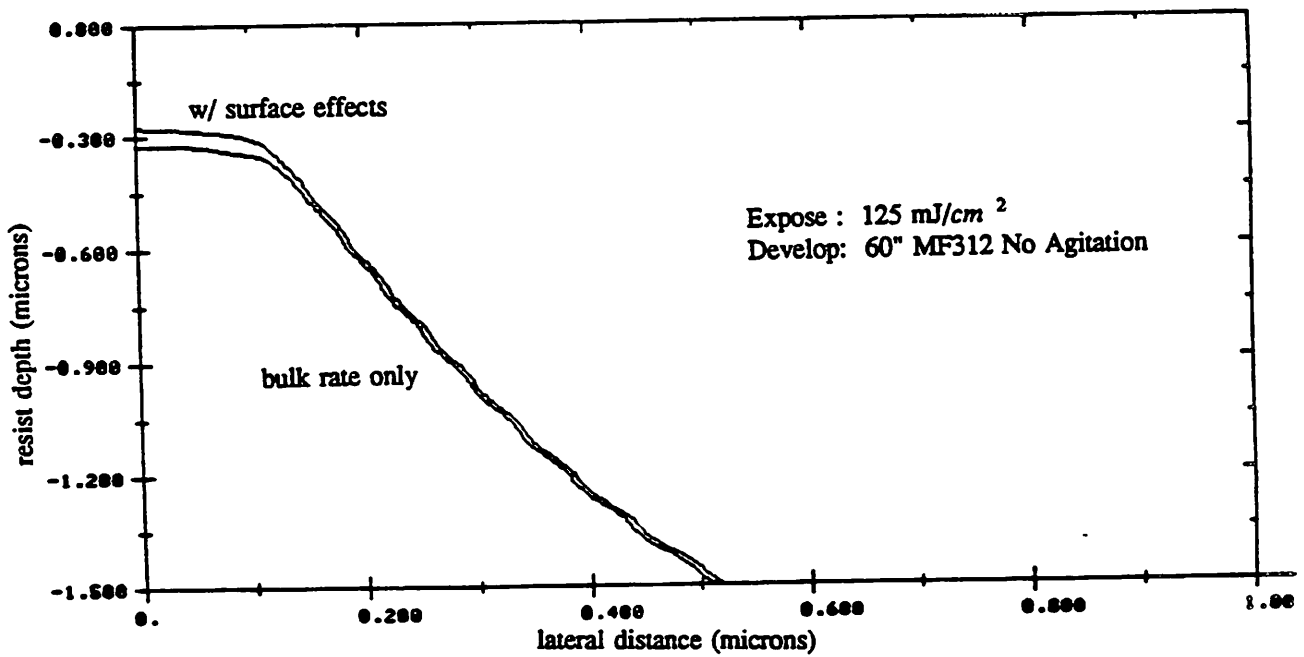
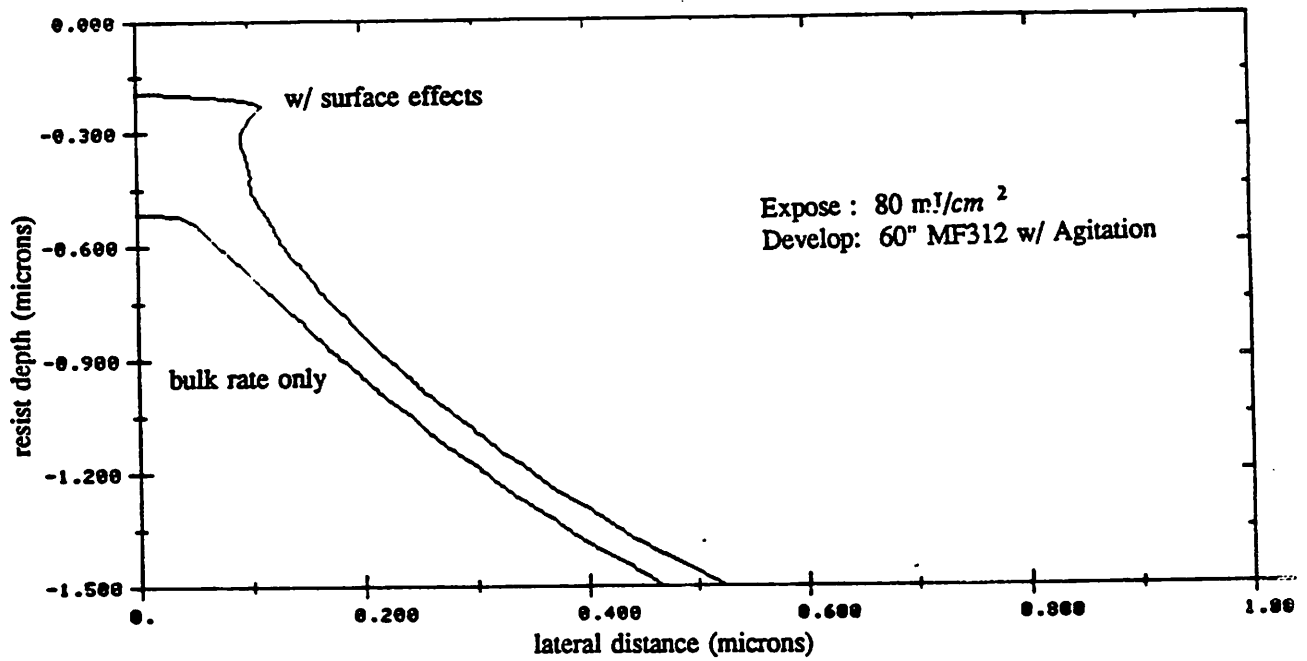


Figure 4.8 SAMPLE profile for MF312 developer using 3 rate parameters (bulk rate) and 6 rate parameters (including surface retardation effects)

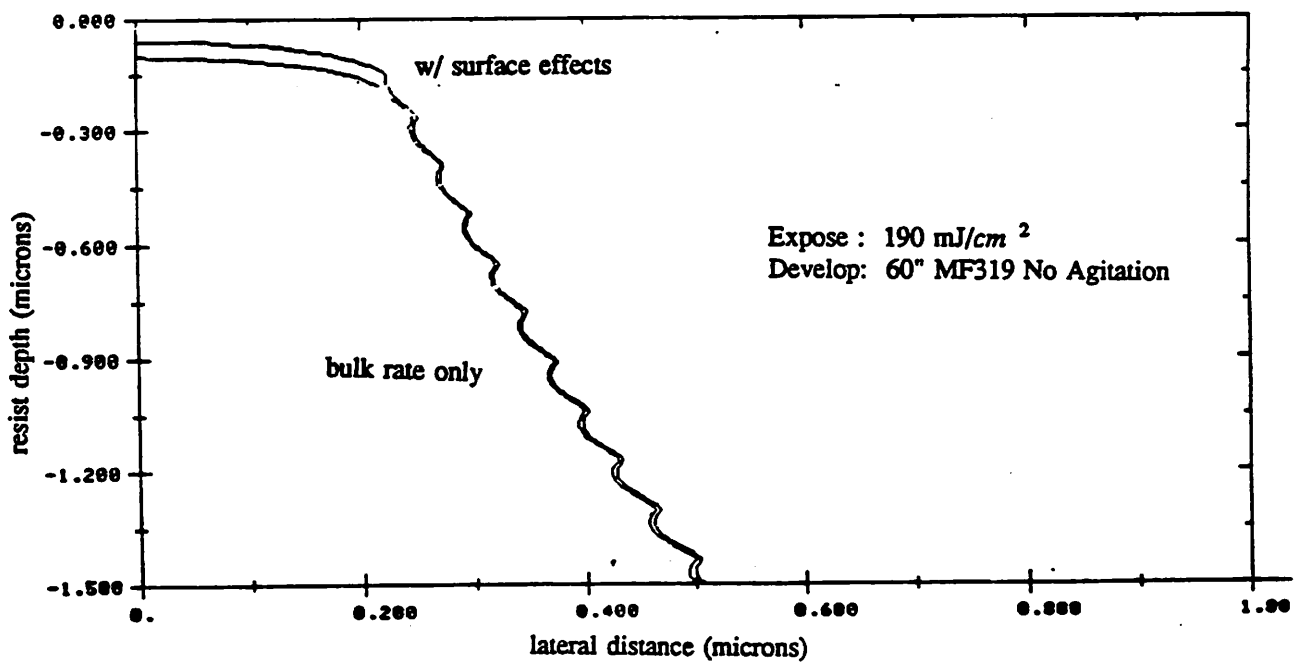
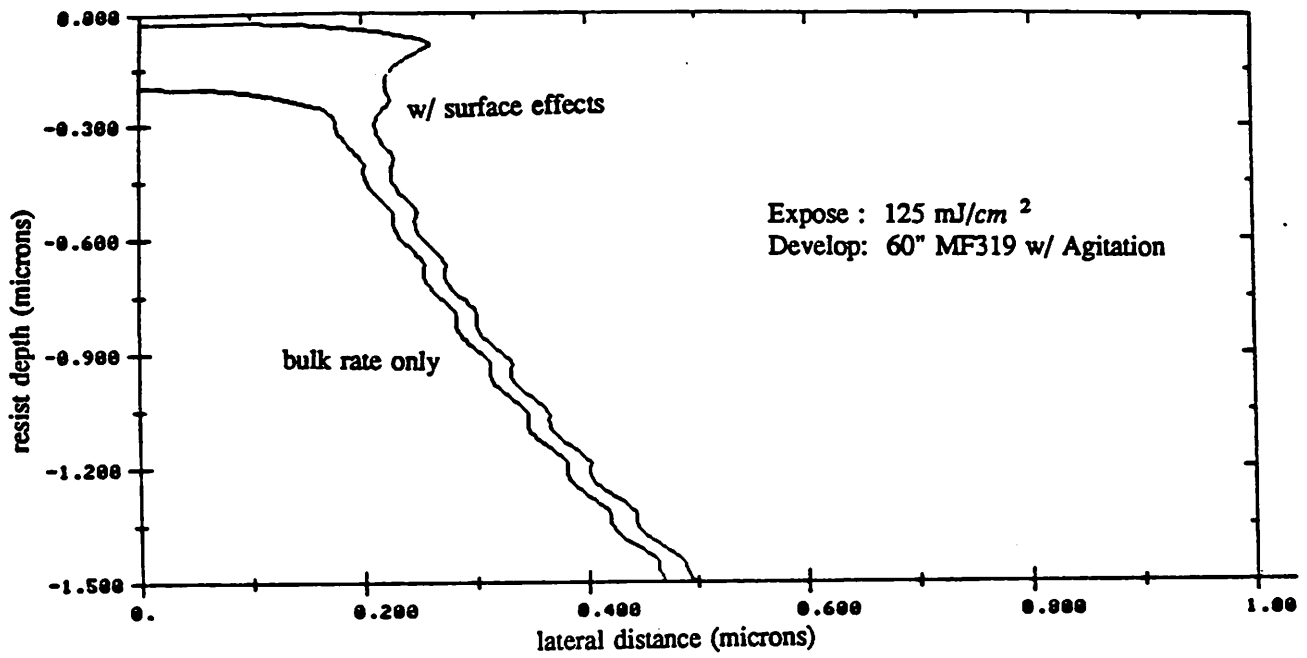


Figure 4.9 SAMPLE profile for MF319 developer using 3 rate parameters (bulk rate)
 and 6 rate parameters (including surface retardation effects)

Table 5. Dose Requirement for 1 μm line/space pattern

| Developer | Agitation (mJ/cm^2) | No Agitation (mJ/cm^2) |
|--------------------------------|---|--|
| MF312 | 81 | 125 |
| MF314 | 92 | 90 |
| MF319 | 125 | 190 |
| 0.15N KOH | 135 | 165 |
| 0.15N KOH w/ 400ppm FSC | 135 (bulk rate) | - |

Surface Tensions of ZONYL® Fluorosurfactants in 10% Potassium Hydroxide

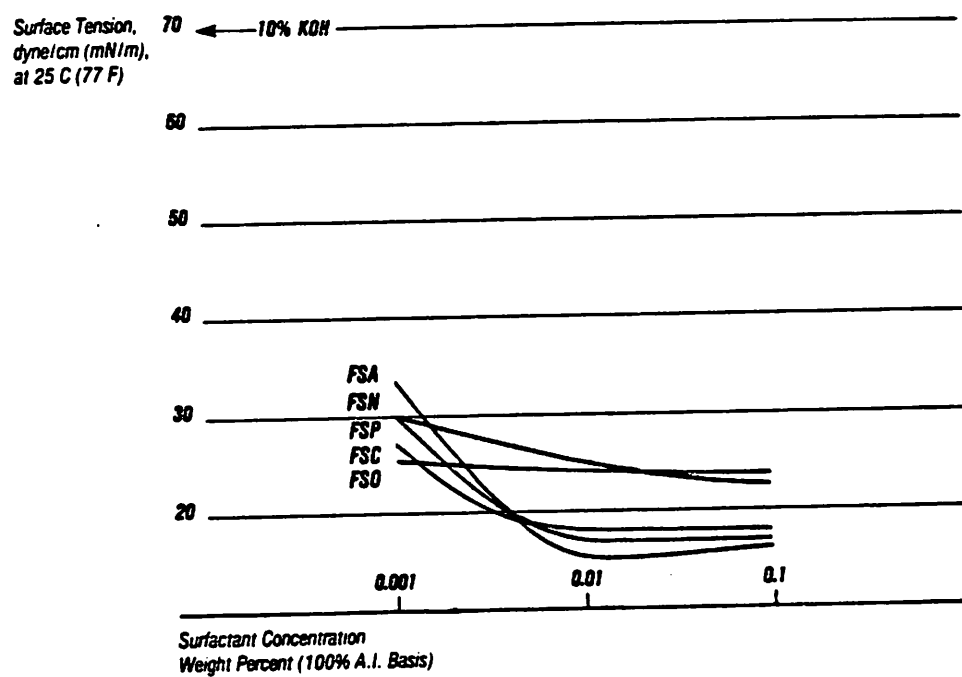


Figure 5.1 Effect of surfactants on reducing surface tension in 10% KOH

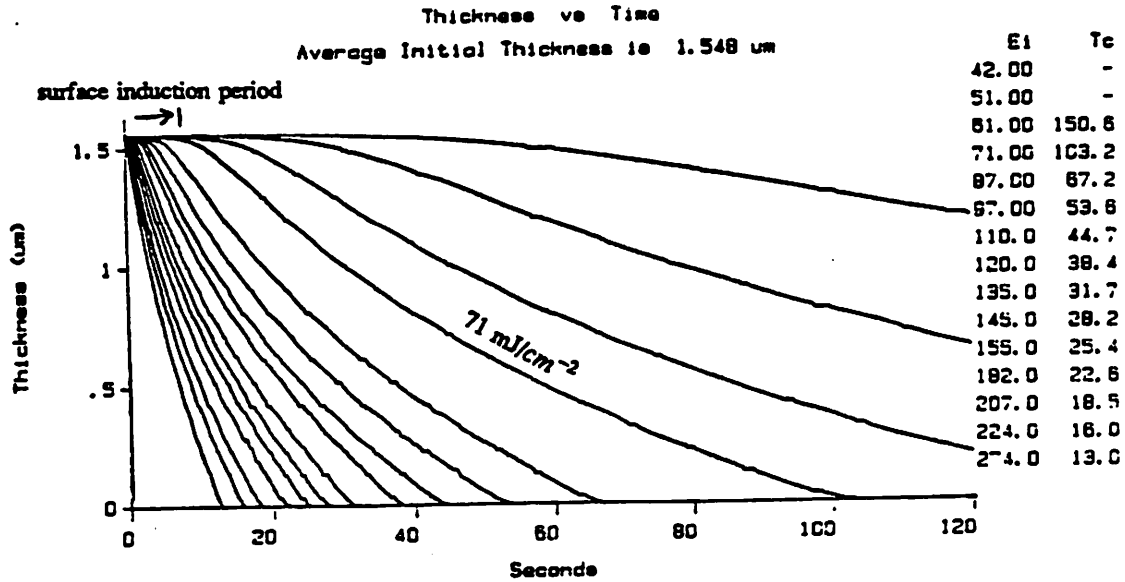
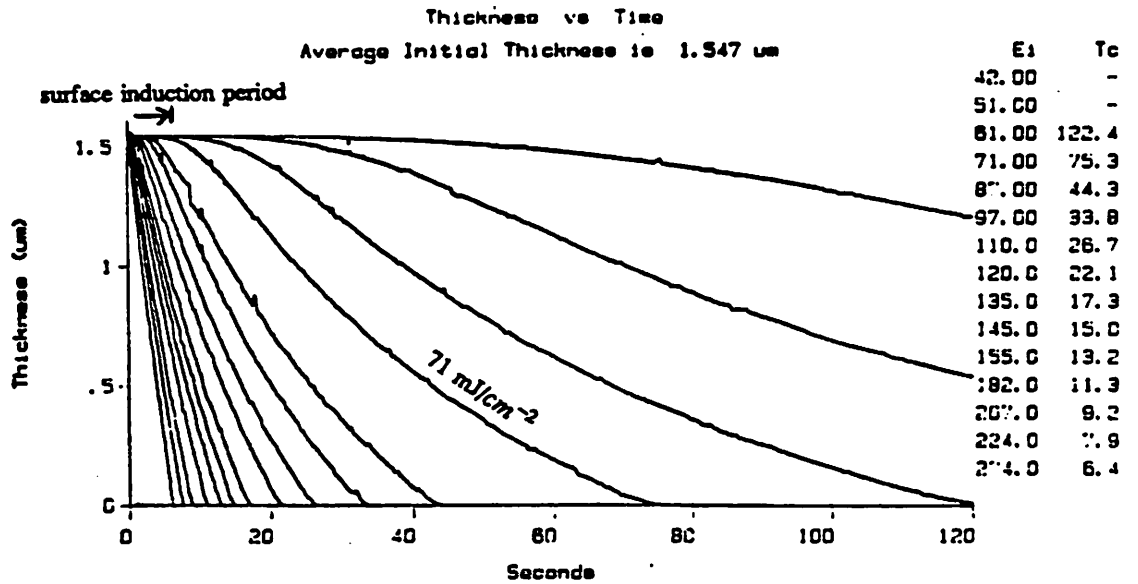


Figure 5.2 Surface retardation effect for development in KOH with (top) and without agitation (bottom)

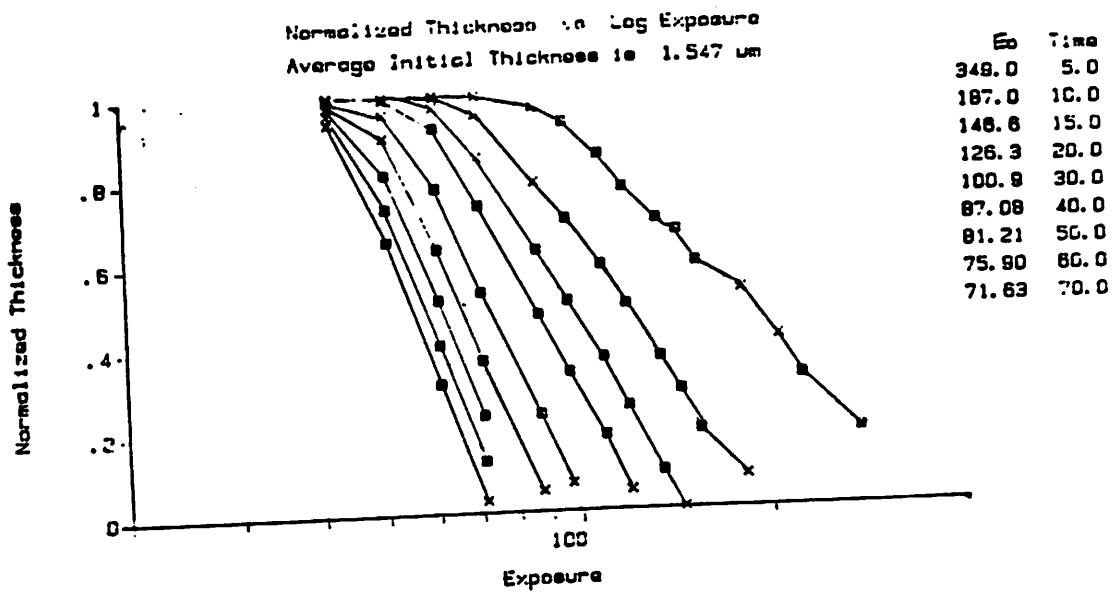
Process Conditions:

Resist : Shipley 1400-31

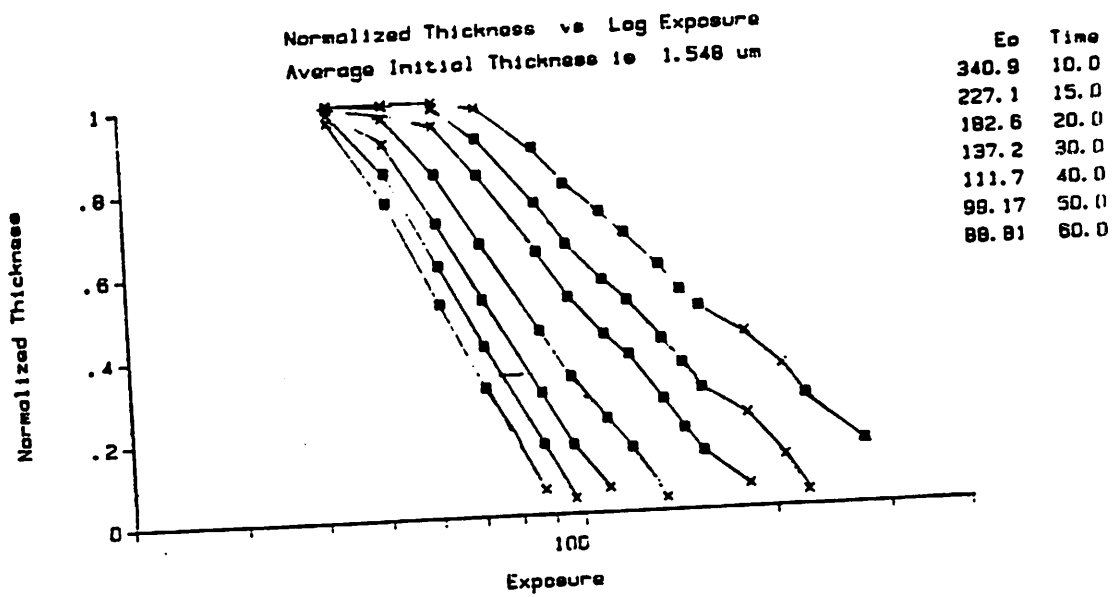
Prebake: 110 deg C hotplate, 60 sec

Expose : 42 - 274 mJ/cm^2

Develop: 0.15N KOH



Gamma
1.69 2.50 2.80 2.92 3.52 4.09 4.03 4.23 4.41



Gamma
1.46 1.79 1.97 2.30 2.68 2.87 3.15

Figure 5.3 Comparison of contrast for agitated (top) and unagitated (bottom) development in 0.15N KOH

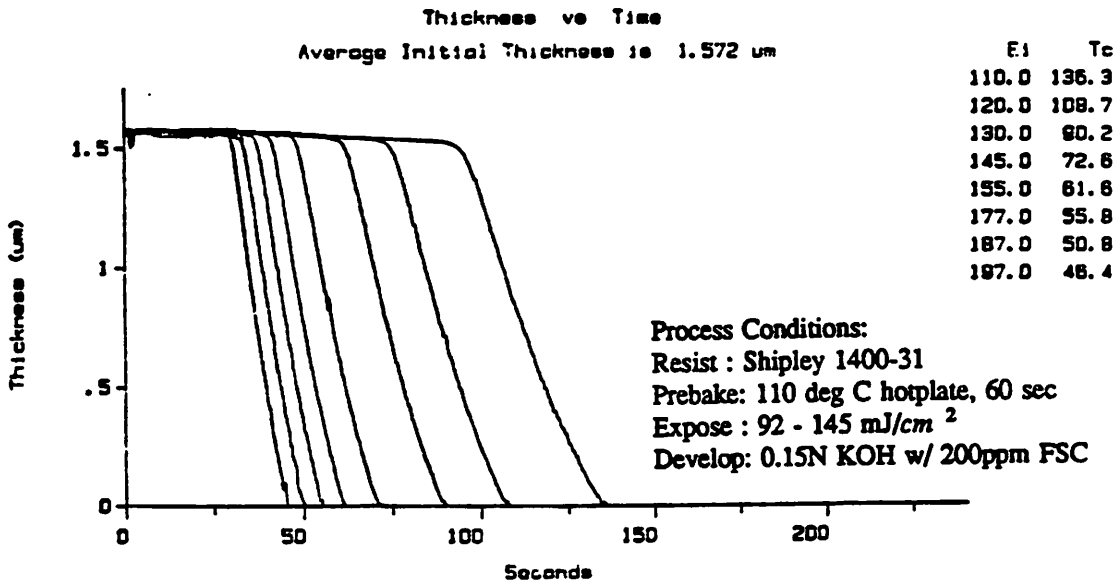
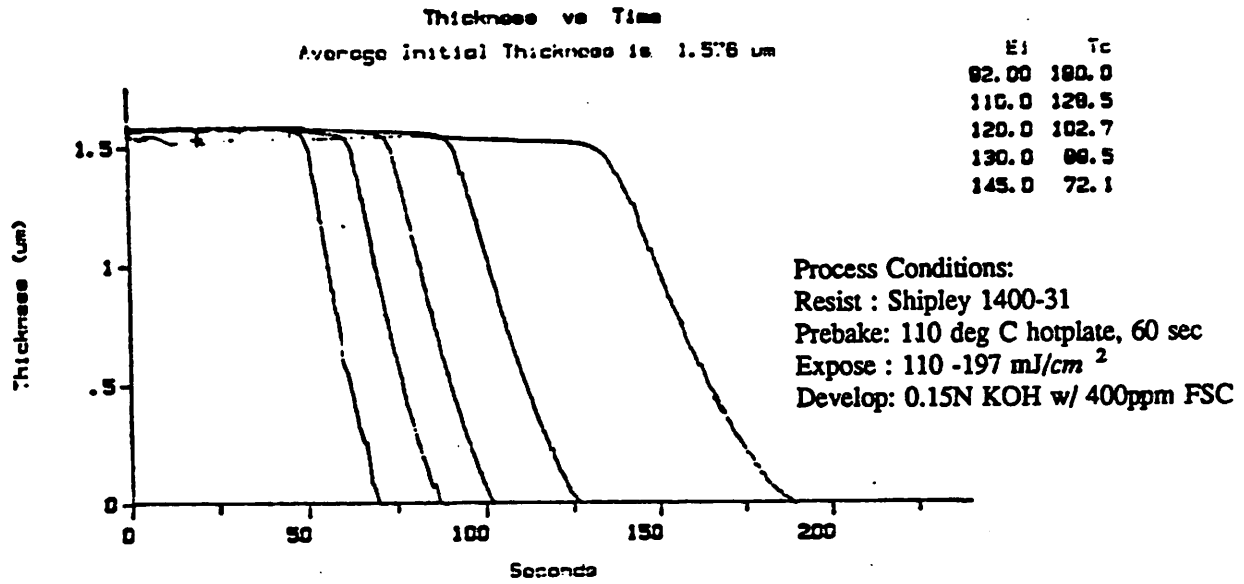


Figure 5.4 Strong surface retardation effect for development in KOH with FSC surfactant

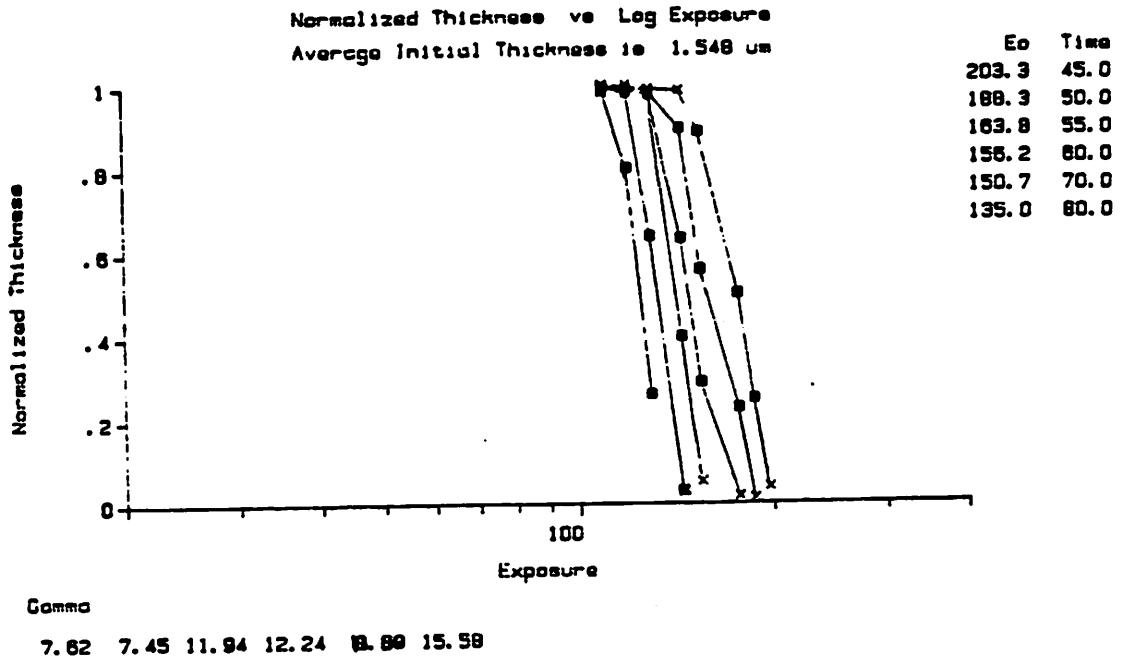
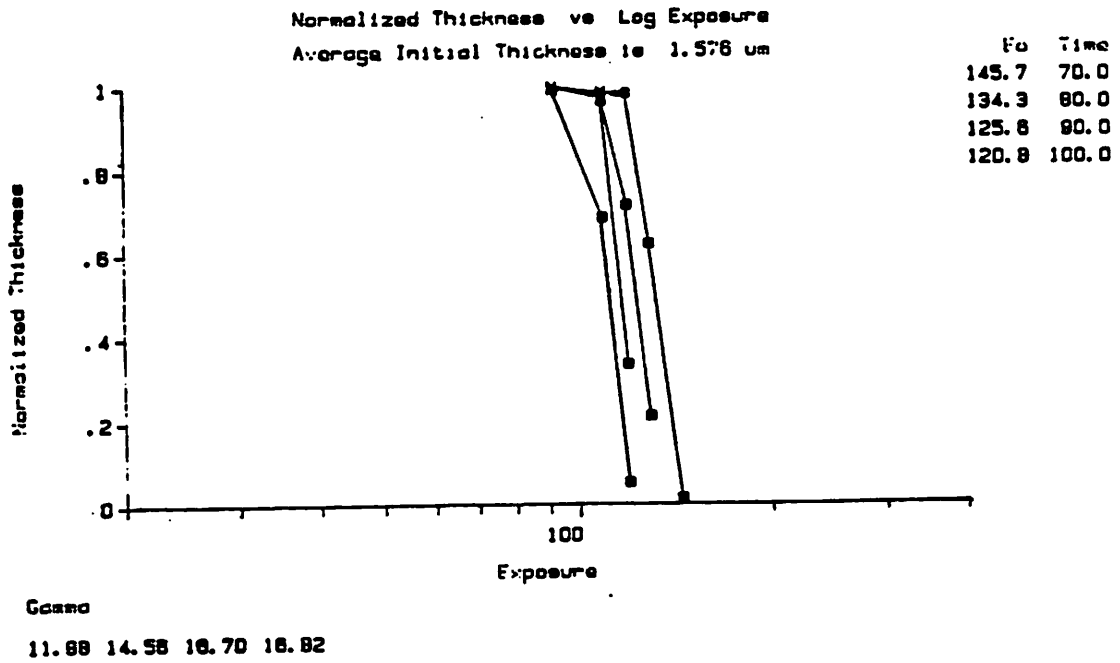


Figure 5.5 Contrast Enhancement by adding 200ppm (top) and 400ppm (bottom)
FSC to 0.15N KOH developer

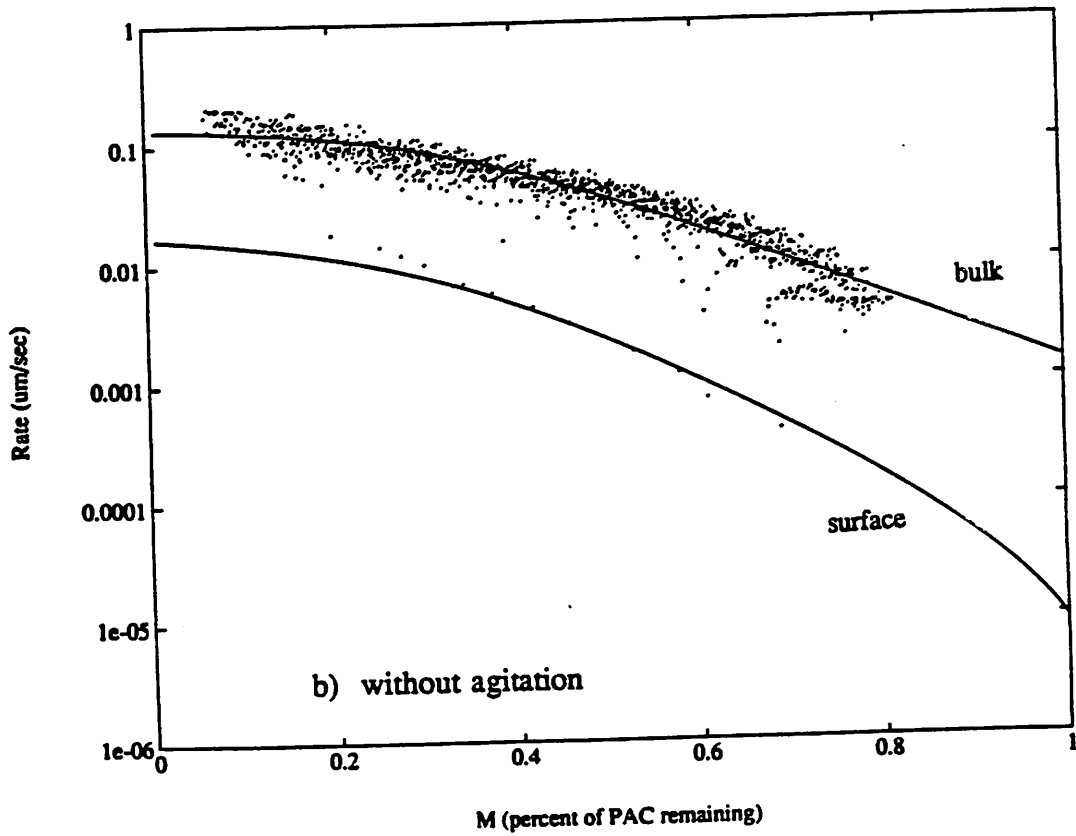
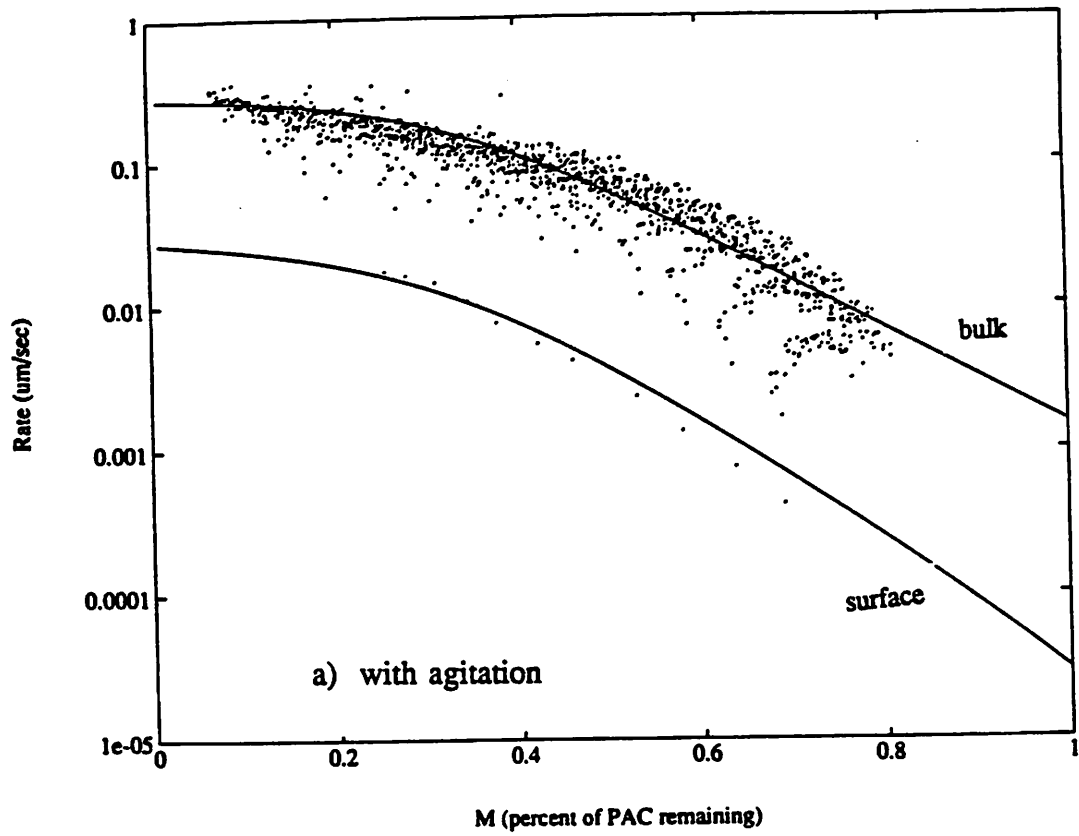


Figure 5.6 R vs M plots for 0.15N KOH

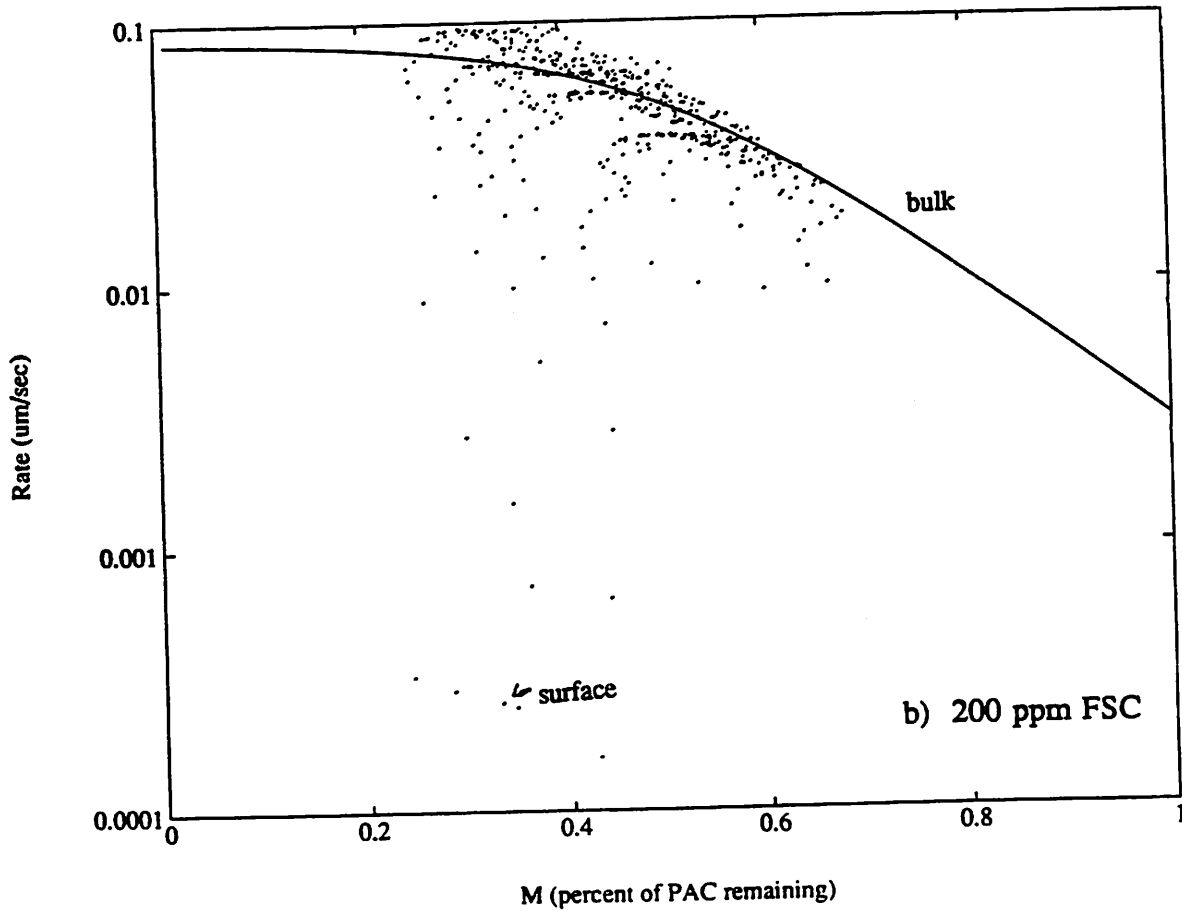
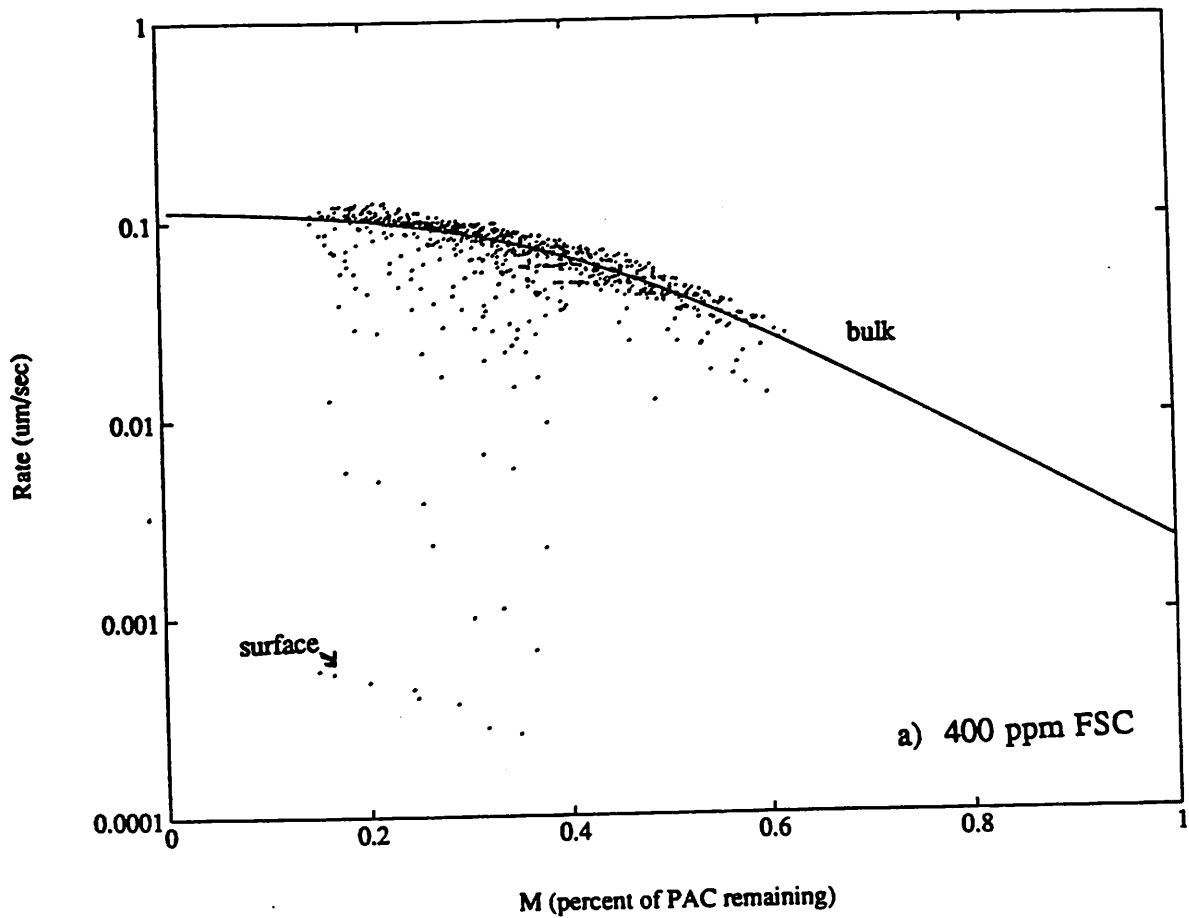


Figure 5.7 R vs M plots for 0.15N KOH with FSC surfactant

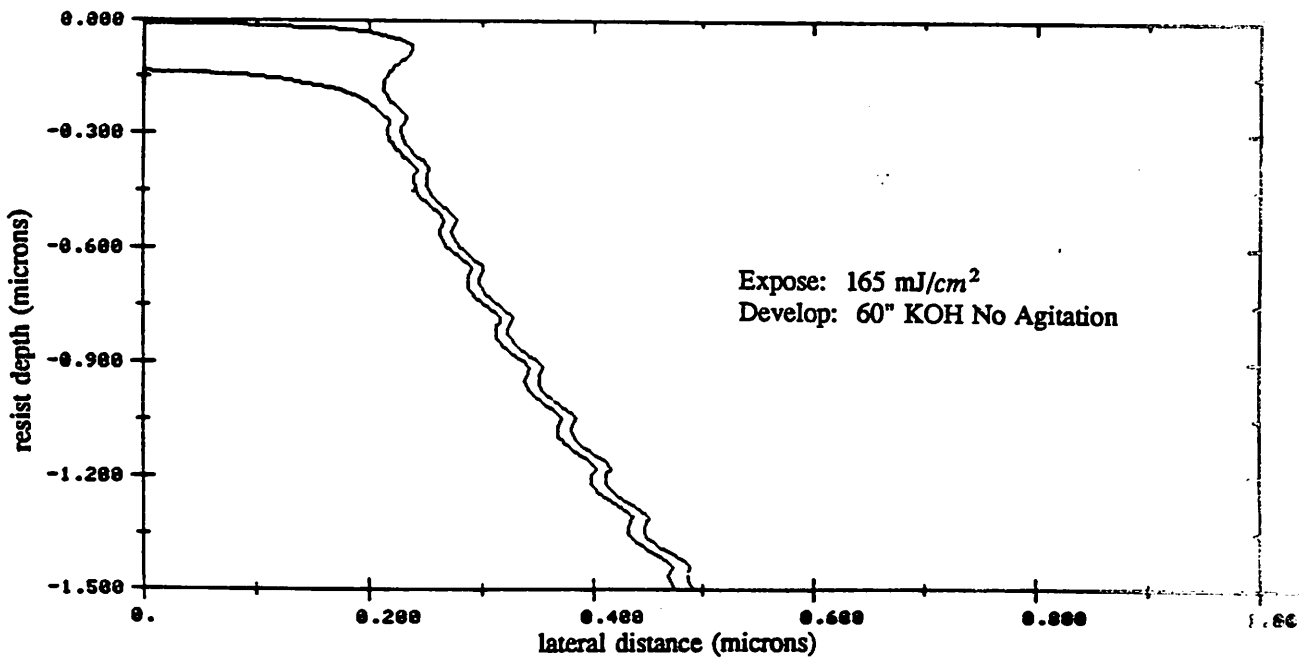
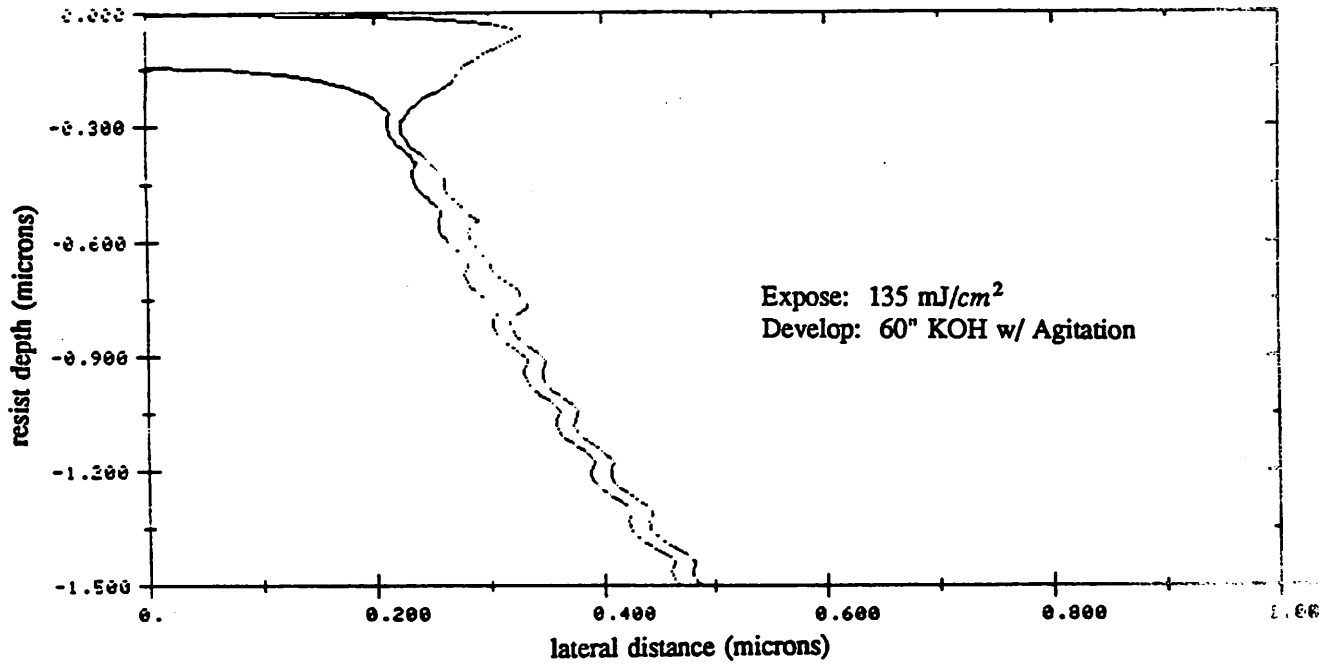


Figure 5.8 SAMPLE profile for KOH developer using 3 parameters (bulk rate)
and 6 parameters (including surface retardation effects)