# EUV Resist Outgassing

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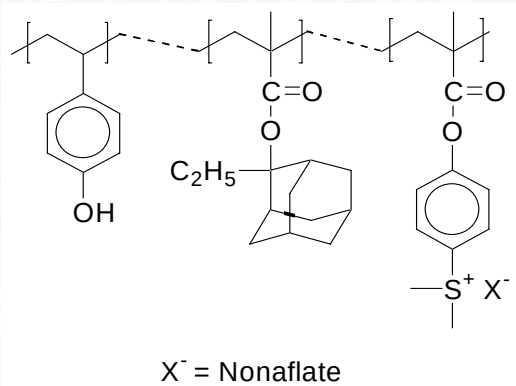
# Objectives

- **Screen resists before they are used on SEMATECH's microexposure tools**



SEMATECH EUV Resist Test Center

- **Learn how polymer-bound photoacid generators (PAGs) affect outgassing**



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# Previous Results

- Most outgassed species are products from acid-catalyzed or photochemical cleavage of protecting groups and decomposition products from the PAG[1]
- Outgassing amount correlates to resist type[2]
  - Low outgassing: DQN and annealing positive CA resist
  - High outgassing: Negative tone CA and non-CA resist
- EUV outgassing is higher than193nm or 157nm outgassing[3]
- ESCAP resists show crosslinking at low doses and scissioning at high doses[3]
- Resists with high $E_a$ and non-ionic PAGs show lower outgassing[4]
- Outgassing limit for Intel microexpsoure tool is 6.5E+13 molecules/$cm^2$ [4]


1) Nealey, P. et al., J. vac. Sci. Technol. B 18(6), Nov/Dec 2000.
2) Watanbe, T., et al., J. vac. Sci. Technol. B 19(3), May/June 2001.
3) Domke, W-D., et al., SPIE, Vol. 5753, 2005.
4) Yueh, W., et al., SPIE, Vol. 5753, 2005.




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# Experimental Details

- A resist coated wafer is introduced into the chamber and pumped down.
- The wafer is exposed to EUV light, then the chamber is purged with $N_2$ into the absorption tube.
- Repeat with 2 more wafers to obtain adequate signal.
- Send absorption tube to independent analytical laboratory for gas chromatography/mass spectroscopy analysis.
- Absorption tubes are packed with Carbotrap 300 multimedia bed.



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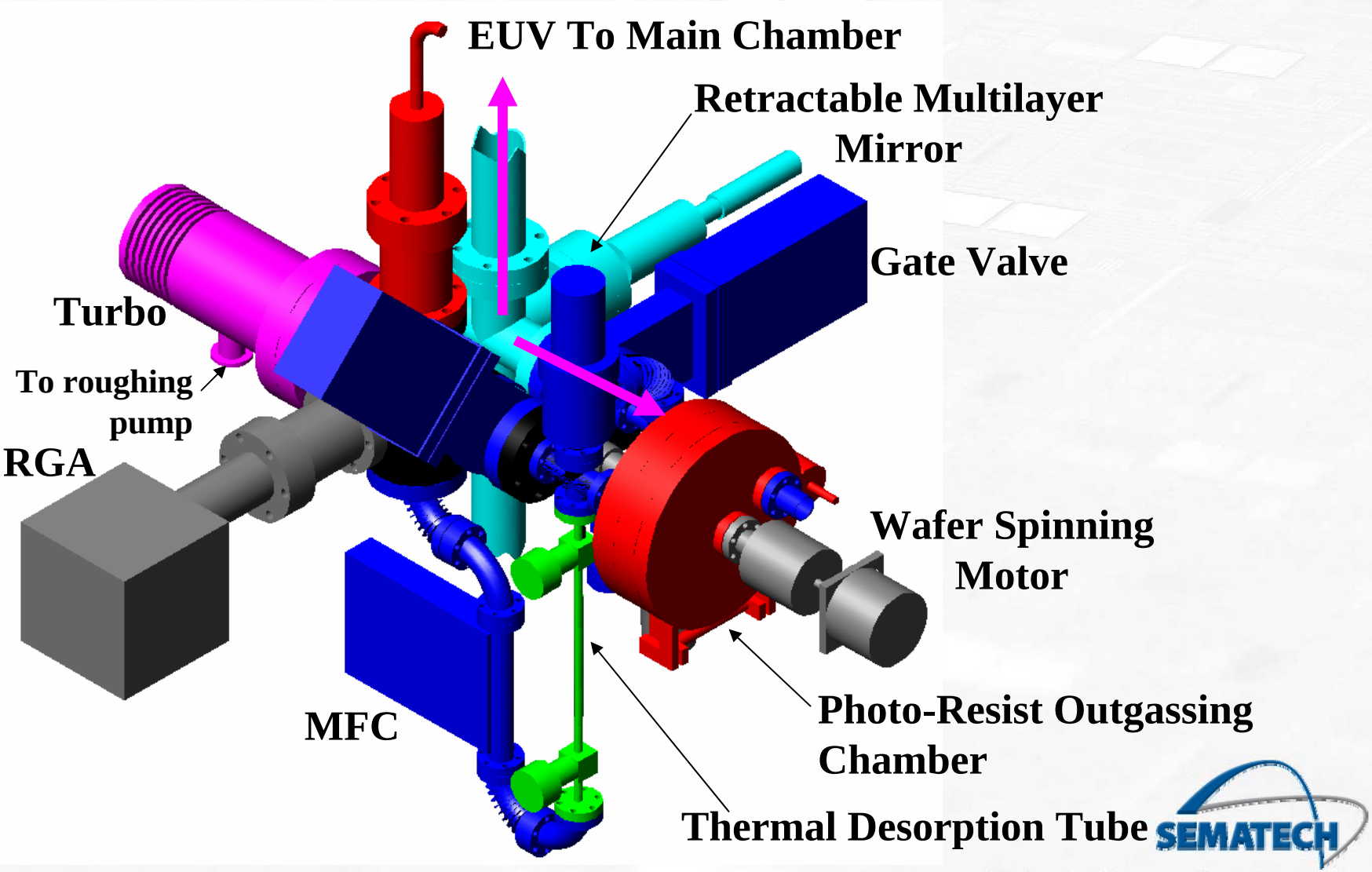
# Wisconsin EUV Exposure Chamber
## Synchrotron Source



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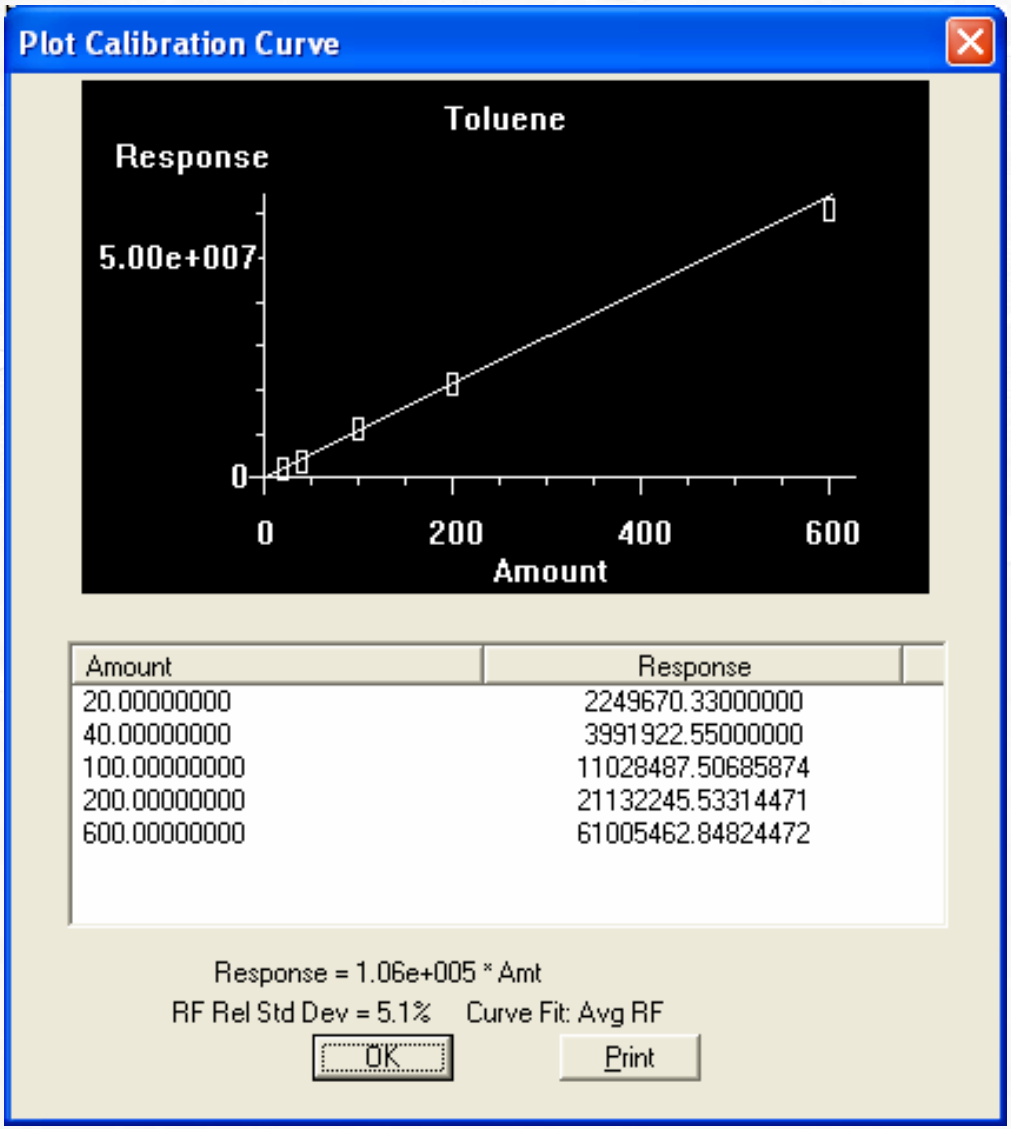
# Calibration of GC/MS with Toluene




| Amount | Response |
|---|---|
| 20.00000000 | 2249670.33000000 |
| 40.00000000 | 3991922.55000000 |
| 100.00000000 | 11028487.50685874 |
| 200.00000000 | 21132245.53314471 |
| 600.00000000 | 61005462.84824472 |

Response = 1.06e+005 * Amt

RF Rel Std Dev = 5.1% Curve Fit: Avg RF

OK Print

## GC/MS Details:

- Agilent 6890 GC
- Agilent 5973 MSD
- GC/MS calibrated with toluene down to 5ng, 5.1% RSD
- Hydrocarbons quantitated as toluene
- Scan range 35- 435 amu



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# Conversion of GC/MS Data to Molecules/cm$^2$

- Total hydrocarbons are calculated from total peak area of chromatogram and toluene response factor; reported in units of $\mu$g/m$^3$.

- Units are converted to molecules/cm$^2$ with the molecular weight of toluene, flow rate of $N_2$, and the exposure area.



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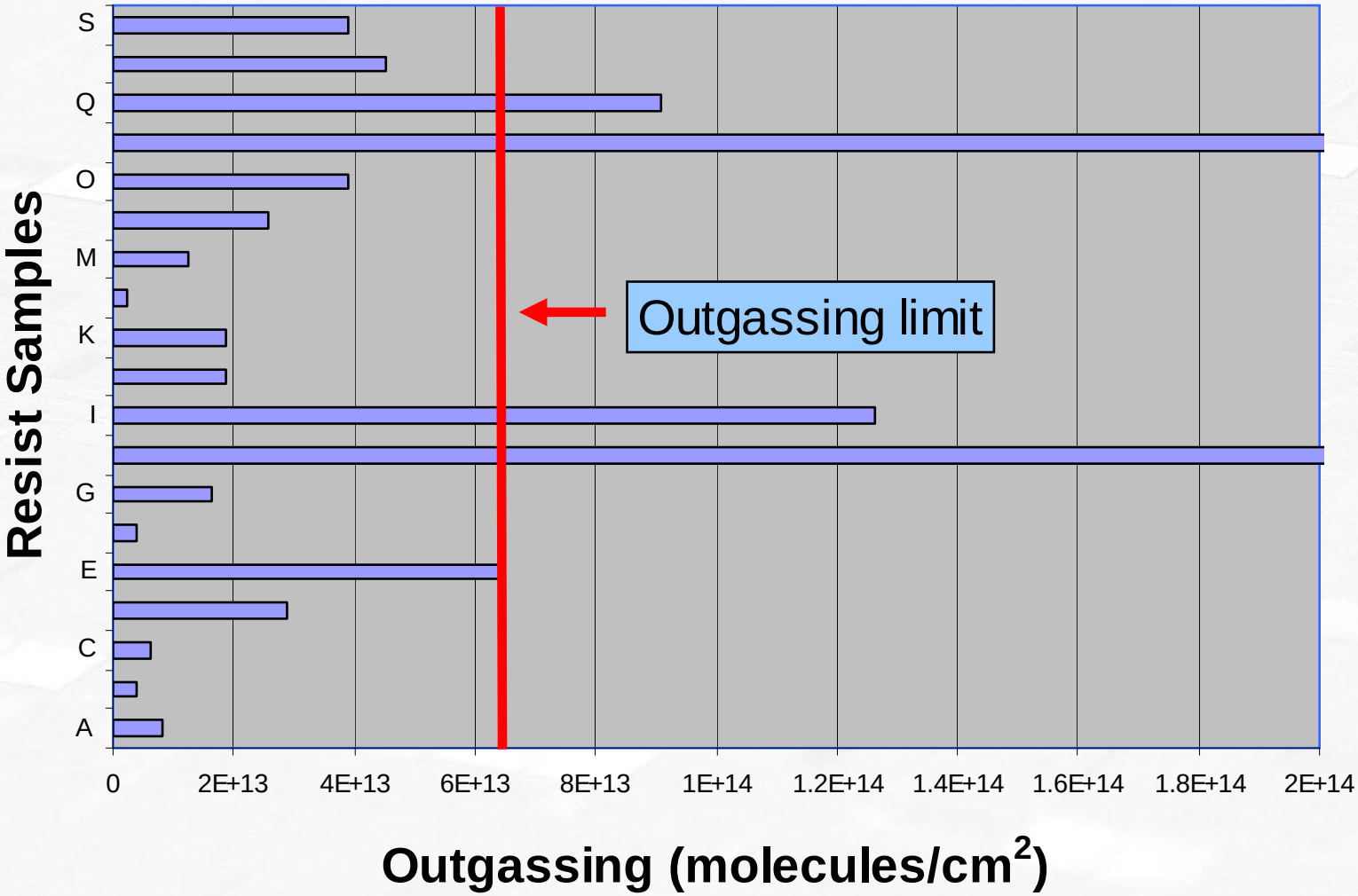
# Outgassing Results




**Most resists meet the requirement.**



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# Outgassing Observations

- The majority of outgassed species are related to the PAGs or the deprotecting groups.
- The most common outgassed PAG species is benzene unless the PAG is incorporated into the backbone or a non-ionic PAG is used.
- The common outgassing deprotecting groups are 2-methyl-1-propene, 2-methyl-2-propanol, adamantane or naphthalene byproducts.
- Low $E_a$ resists outgas more than high $E_a$ resists.



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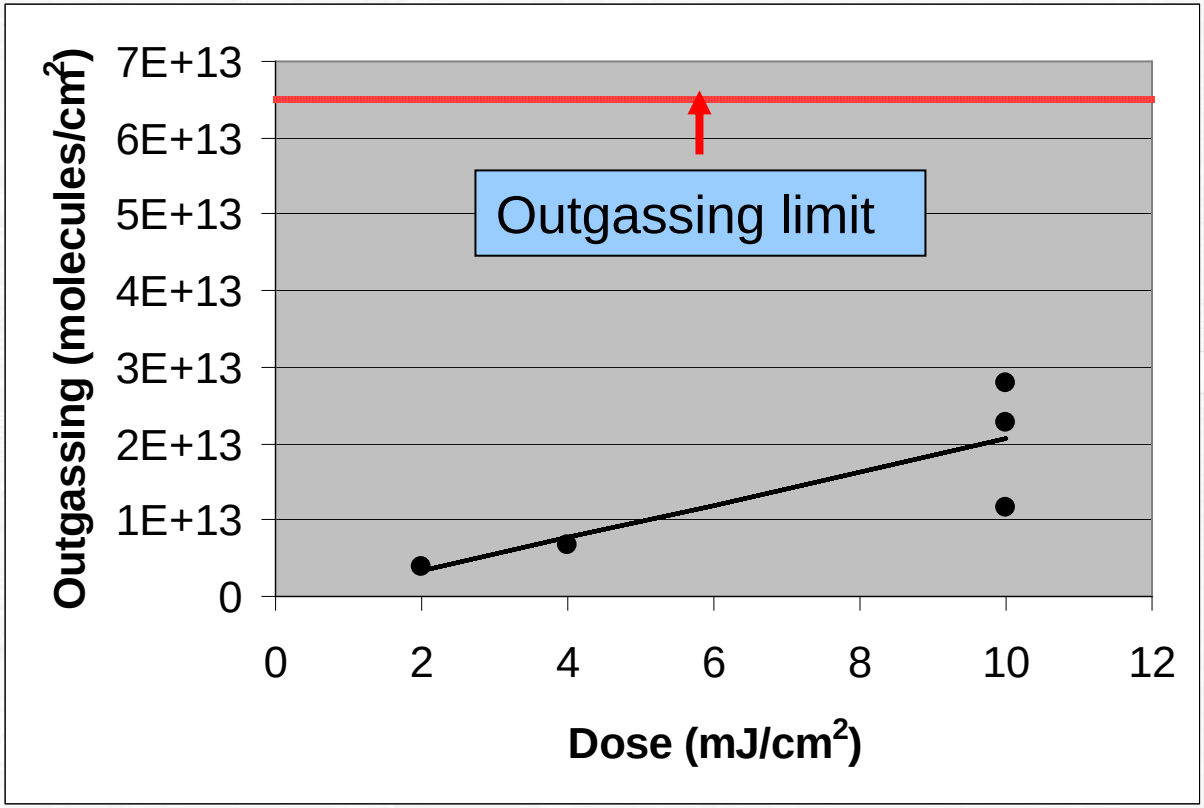
# Outgassing versus Exposure Dose




**Resist F**

- **Outgassing increases with increasing dose.**
- **Repeated measurements at 10mJ/cm$^2$ on 3 different days show variation in outgassing.**



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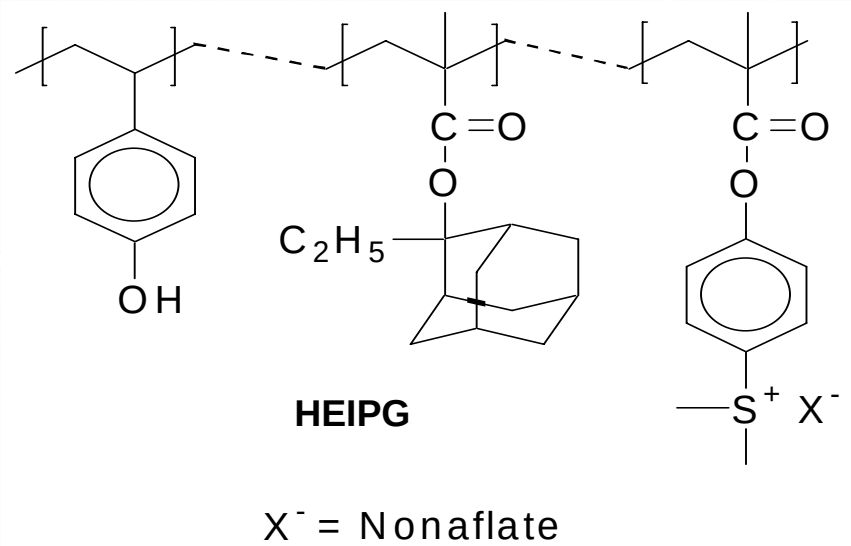
## Polymer-Bound Photoacid Generators*




**Polymers were synthesized to test effect of polymer-bound PAGs on LER and photospeed.**

poly (HOST-co-EAMA-co-PAG)
45% HOST, 50% EAMA, 5% PAG

***Project funded by SEMATECH**

**Reference: K. E. Gonsalves, M. Thiyagarajana, K. Dean, P. Santiago, L. Rendón, A. Jeyakumar, C. L. Henderson, Advances in Resist Technology and Processing XXII, Proceedings of SPIE Vol. 5753, 467-475.**



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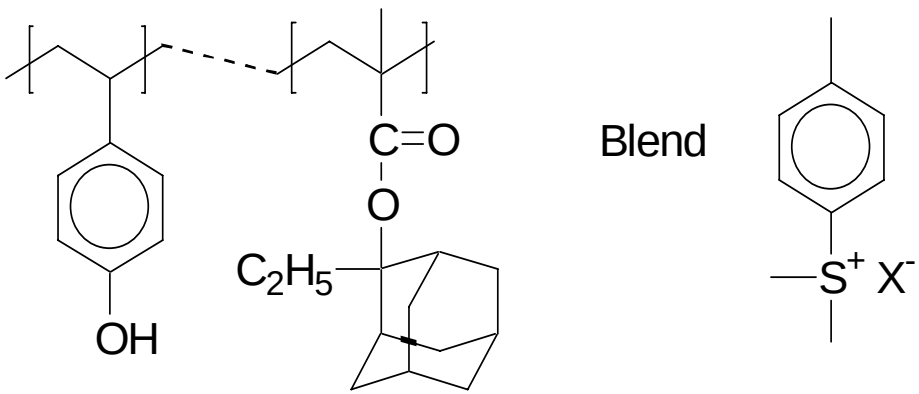
# University of North Carolina at Charlotte

## Polymer-Bound Photoacid Generators




**HE(Nf)**

$X^-$ = Nonaflate

**Control polymer was made to test the effect of polymer-bound PAGs on LER and photospeed.**

poly (HOST-co-EAMA) blend PAG (Nf)
45% HOST, 50% EAMA, 5% PAG



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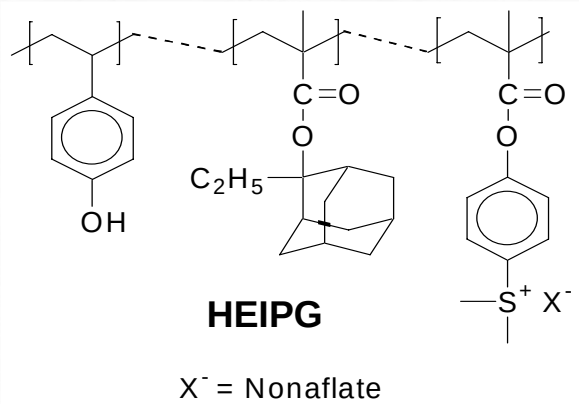
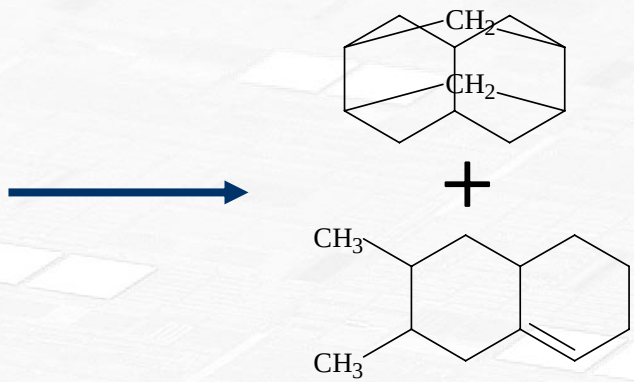
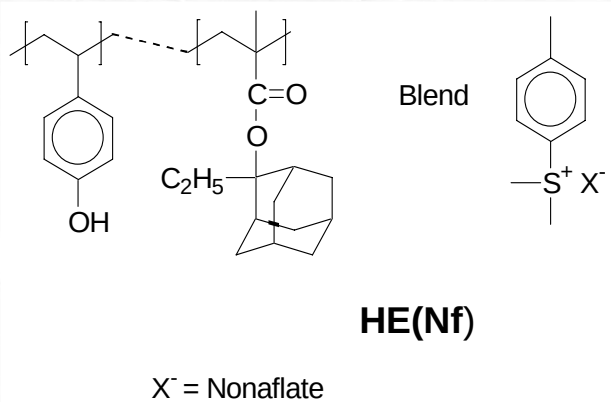
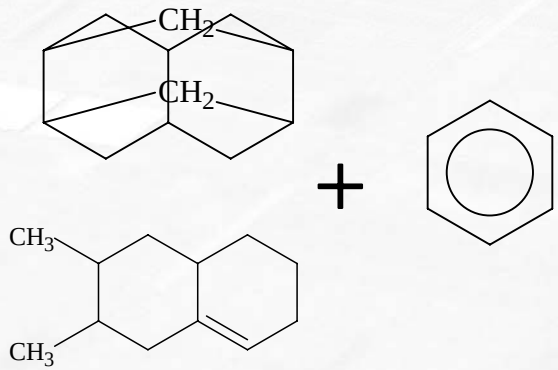
# UNCC Resist Outgassing Products




**No Benzene!**




- **The polymer-bound PAG did not outgas PAG by-products.**
- **The adamantyl blocking group rearranges into 2 outgassing products.**



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# Conclusions

- Outgassing methodology has been established to determine qualitative and quantitative data.
- Outgassing increases with increasing dose for a particular resist.
- Polymer-bound PAGs might provide route for lower outgassing resists.
- Low $E_a$ resists outgas more than high $E_a$ resists.



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# Future Work

- Continue to improve system repeatability.
- Investigate polymer structure influences on outgassing using model polymers.
- Complete outgassing round robin where seven researchers from around the world test the same sample and compare results (with IEUVI Resist Technical Working Group).
- Work on common methodology with other researchers so outgassing rates can be compared (with IEUVI Resist Technical Working Group).



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# Acknowledgements


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- Resist suppliers




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