Formulation of Photoresists - Generic Scenario for Estimating Occupational Exposures and Environmental Releases

-Draft-

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1. Explanatory Notes

This Scoping document draft for the scenario on Photoresist Formulation incorporates review comments on the July 2005 draft. Review comments were received from Canada, Britain and Germany. Primary changes in this draft are in sections 4.0, and 7.0. These reflect new information on resist production volumes and resist compositions.

OR (for the first draft)

The development of a scenario for the photoresist formulation industry will supplement the existing scenario, “Photoresist Use in the Semiconductor Industry”. Photoresists are used in the manufacturing of printed circuit board, optical photographic films, X-ray films and various electronic components. Much of the new chemistry development activities are, however, are for application in the semiconductor industry.

The photoresist manufacturing industry is relatively small in terms of the volume of products produced and in terms of the number of plants worldwide. Life cycle of a chemical in the photoresist involves synthesis of the new chemical, its use in the formulation of the photoresist, the application of the resist in semiconductor production and the disposal of the spent resist.

2. Introduction

Industry: Photoresists are used in the manufacture of camera film, printed circuit boards, electronic components and semiconductors. Developments in new chemistries for the semiconductor manufacturing has been the most dynamic. The industry catering to the semiconductor manufacturing market is relatively small in terms of the number of plants and in terms of the volume of the chemical produced. Resist coating on a typical 300 mm silicon wafer uses between 2 to 5 ml per application. A single wafer goes through several resist applications as multiple levels of circuits are created.

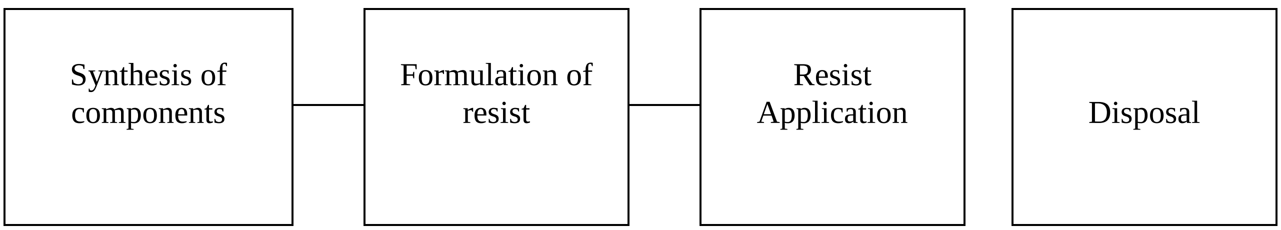
Technology: Photoresists for semiconductor manufacturing application need to be nearly free of particulate and trace metal contaminations. Nearly all state of the art resists are formulated and handled in closed environment. Photoresists contain resin or polymers, sensitizers, solvents, surfactants and other additives for anti reflective properties. Resins or polymers are received from suppliers in solid or solution form. Sensitizers usually are received or stored as solids. Other additives are added in less than 1% range each.

Process: The process of resist formulation involves mixing (dissolving solids), filtration and packaging. Occupational exposures occur in loading, filter cleaning, equipment cleaning and container cleaning. Filters and cleaning waste material is generally packaged as hazardous waste to be land-filled or incinerated.

3. Scope

Scope of this document is limited to the formulation of photoresists. Photoresists include positive and negative type and sensitive in optical, e-beam, and X-ray radiation sensitive resists. The scope also includes ancillary chemicals such as anti reflective coatings. The 'Formulation' includes the formulation, filtration and packaging. Synthesis of any component is not included in this scenario. Synthesis of a new chemical is specific to each new chemical and therefore inclusion of synthesis in the generic scenario is not feasible. The application of the resist is covered under the scenario, "Photoresist Use in the Semiconductor Manufacturing" which includes the disposal part of the resist life cycle.

Photoresist Life Cycle



Photoresist Formulation, Filtration and Packaging Process

The production of photoresists involves blending of sensitizers, resins, solvents and additives in reactors or mixing vessels. The formulated product is filtered. Generally several filter changes are required to achieve low trace metals and low particulate contamination levels.

Packaging is done in clean class environment. The packages include one and four liter bottles, and one liter, four liter and 20 liter Nowpaks. Nowpaks have become popular for maintaining resist cleanliness. Nowpaks are collapsible Teflon bags inside a rigid polyethylene bottle. They are designed to collapse as the resist is used on the tool and designed to leave relatively smaller amount of residue. Spent Nowpaks are collapsed and sent out as hazardous waste either to be land filled as hazardous waste or to be incinerated.

Reactors/mix vessels are cleaned in between the batches unless another batch of the same chemistry is to follow. Cleaning of vessel is done using 'piped in' solvents. Filter change is a manual operation.

Life cycle of photoresist includes the resist formulation, its application on silicon wafers, printed circuit boards or other electronic components and its disposal as waste. An emission scenario document for photoresist use in semiconductor industry was released in 2004. 100% of the photoresist applied to silicon wafers is removed in subsequent operations. It does not become part of any product.

Solvent(s) make up about 60% of the resist formulation. Depending upon size of a plant, solvents are either piped into the mixing vessels or manually transferred using pumps or nitrogen pressure.

Solid resins, photoactive compounds and polymers are received in 20 kg to 200 kg paper fiber drums.   The solids are generally manually weighed and transferred to the mixing vessels. Many plants receive pre-weighed quantities from the supplier to minimize or eliminate manual weighing at the point of use.

Mixing is performed in closed mixing vessels. The formulated liquid resists is pumped/recycled into the mixing vessel through the filters. The filter recycling is done several times for a batch using progressively smaller size filters.   The filtered product is pressure fed or pumped to a bottling station. Bottling station is generally a clean exhaust hood. The operation may be automated with minimal operator contact at larger plants.

Semiconductor industry experiences significant periodic upward and downward trends and photoresist production volumes reflect these unpredictable variability.

Photoresist Composition – Default Values

Component	**DNQ-Novolac resists**	**Chemically Amplified resists**	**DUV**
Solvent	70%	80%	80%
Photoactive Compound	8%		
Polymer	22%	20%	20%

Environmental release points and operator exposures points

Solvent(s) make up between 60% to 80% of the resist formulation. Depending upon size of a plant, solvents are either piped into the mixing vessels or manually transferred using pumps or nitrogen pressure.

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The environmental release and operator exposure points are:

- Solid powder into the air during the weighing - dermal and inhalation exposure
- Solid powder into the air during transfer from drum to mixing vessel – dermal and inhalation exposure
- Liquid vapors into the air during filter changes – dermal and inhalation exposure
- Liquid vapors into the air during bottling operation – dermal and inhalation exposure
- Liquid photoresist into the waste stream, generally collected and handled as a hazardous waste, as a result of mixing vessel and filter equipment cleaning - Dermal exposure from filter and packaging equipment cleaning.

Semiconductor industry is unique in terms of production volume variability from year to year. It is an industry that experiences significant periodic upward and downward trends and photoresist production volumes reflect these unpredictable variability.

Industry Data

U.S. Photoresist Production (per year)

	1999	**2000**	**2001**	**2002**	**2003**	**2004**
$Millions	690	835	650	680	745	850
Gallons						

Production Data

Parameter	**DNQ/Novolac**	**DUV**	**Chemically Amplified**
Annual Production			
# of U.S. Formulators/Plants			
Operating Days			
# of shifts			
Batch size			
Batch Cycle - days			

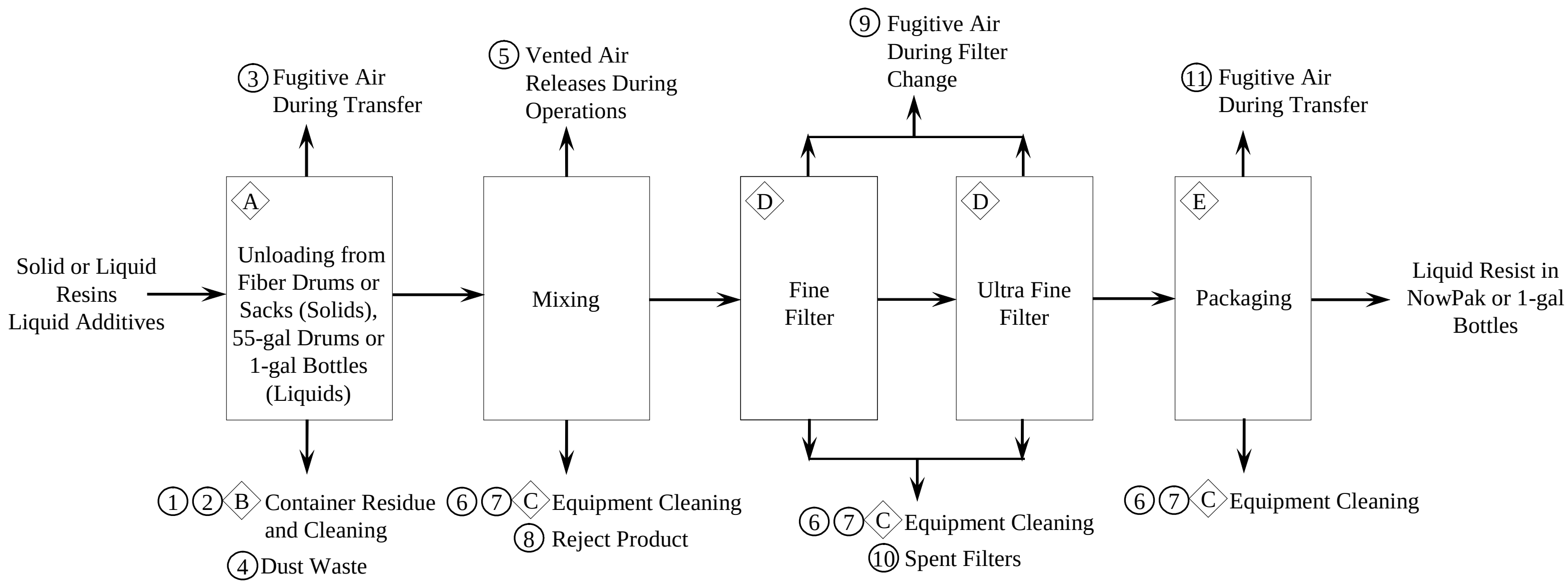
Environment Release Estimates

Operation	**Air**	**Water**	**Land**
Solids Charging	x	x	x
Solvent Charging	x		
Filter Change	x		x
Filter housing cleaning	x		x
Vessel Cleaning	x		x
Bottling	x		
Bottling equipment cleaning	x		x
Spent Filter disposal	x		x
Spent waste bottles/nowpaks			x

Container Data

Parameter	**Raw Materials**
Resin received	5 gal, 50 gal drums
PAC received	5 gal, 50 gal drums
Solvents received	Piped, 55 gal drums
Photoresist shipped	1 lit and 4 lit bottles
	1 lit, 4 lit and 20 lit Nowpak

Photoresist Formulation Process Flow Diagram



<u>Environmental Releases:</u>

1. Container residues released to water, incineration, or landfill.
2. Open surface losses of volatile chemicals to air during container cleaning.
3. Transfer operation losses to air of volatile chemicals during unloading into the mix vessels.
4. Settled dust collected from the transfer of a solid powder into the mixing vessel released to water, incineration, or landfill.
5. Vented losses of volatile chemicals to air during mixing operations.
6. Equipment cleaning releases to water, incineration, or landfill.
7. Open surface losses of volatile chemicals to air during equipment cleaning.
8. Reject product released to incineration or landfill.
9. Open surface losses of volatile chemicals during filter change.
10. Release of chemicals trapped in spent filters to incineration or landfill.
11. Transfer operation losses to air of volatile chemicals during bottling operation.

<u>Occupational Exposures:</u>

A. Dermal and inhalation exposure from unloading solid and liquid materials into the process equipment.
B. Dermal and inhalation exposure from liquid and solid container cleaning.
C. Dermal and inhalation exposure during process equipment cleaning.
D. Dermal and inhalation exposure during filter change.
E. Dermal and inhalation exposure from bottling operation.

4. Preliminary search sources

EPA
OSHA
NIOSH
OECD
PMN Files
Industry Publications
Other

5 Preliminary search results

These results could be any general industry data. This should not be detailed information. It can include, over all production volumes, number of plants, plant size range, number of workers, any environmental and personal protection controls etc.

6. PMN search results: There were 37 submissions for photoresist chemicals in FY05 and FY06. All 37 submissions reviewed were LVE cases. Two of these cases were consolidated sets of more than one chemical. Three of the 37 submissions were for intermediates.

Chemical Manufacture

- 3 cases were manufactured in the US;
- 1 case was manufactured and formulated into a photoresist solution at the submitter site
- 2 cases were manufactured at the submitter site, but no information was provided on the photoresist formulation operation.

Chemical Import

- 29 cases were imported into the US;
- 18 cases were imported in use-ready photoresist solutions;
- 11 cases were imported for formulation into photoresist solutions in the US;
- 7 cases were formulated at the submitter site
- 4 cases were formulated at unidentified sites not controlled by the submitter:

Additive Function

- 17 cases were photoacid generators;
- 3 cases were resins;
- 3 cases were surfactants and/or leveling agents;
- 2 cases were resolution enhancers;
- 2 cases were coupling agents;
- 1 case was a dissolution inhibitor;
- 1 case was a quencher;
- 1 case was described as a photoactive compound; and

- 2 cases were indicated to be photoresist additives, but their functions were not identified.

Chemical-Physical Properties

- 26 cases were neat solids (one was noted to be a neat solid/paste);
- 6 cases were neat liquids;
- 20 cases were handled only as liquids;
- 12 cases were handled as solids at some point;
- 1 case was volatile (VP > 0.001 torr); and.

Key Results of PMN Database Search

1. The database search generally supports the development of a scenario for the formulation of photoresists; 14 of the 32 cases had US formulation operations, and 6 of the cases were formulated at sites not controlled by the submitter.
2. In general, the number of US formulation sites was known; therefore, the focus of the scenario should be on release and exposure estimates.
3. Attention should be given to releases to incineration due to the use of chemicals containing an element of concern.
4. While most of the cases reviewed were non-volatile (31 of 32 cases), some discussion of volatiles is needed.
5. Exposures to particulate are a concern (12 of 32 cases handled as solids).

7. References