

VENTURA COUNTY AIR POLLUTION CONTROL DISTRICT

**RULE 74.21 - SEMICONDUCTOR MANUFACTURING**

*(Adopted 04/06/93)*

A. Applicability

The provisions of this rule apply to:

1. Any person who utilizes any maskant, developer, or cleaning solvent containing Reactive Organic Compounds (ROC) as part of a semiconductor manufacturing operation.
2. Any person who manufactures or supplies any maskant, developer, or solvent containing ROC sold for use in a semiconductor manufacturing operation in the District.
3. The provisions of this rule shall become effective on September 30, 1993.

B. Operating Requirements

1. No person shall utilize a solvent cleaning station as part of a semiconductor manufacturing process unless:
  - a. All heated or unheated reservoirs, sinks, tanks and containers which transfer, store, or hold ROC containing material are provided with a full cover. Covers must remain closed except while production, sampling, maintenance, or loading or unloading procedures require operator access.
  - b. The freeboard ratio of all heated or unheated reservoirs and sinks holding ROC containing fluids is:
    - 1) Equal to or greater than 0.75 if total facility ROC emissions from semiconductor manufacturing operations are less than 40.82 kilograms (90 pounds) in any month; or
    - 2) Equal to or greater than 1.0 if total facility ROC emissions from semiconductor manufacturing operations are equal to or greater than 40.82 kilograms (90 pounds) in any month.
  - c. In lieu of the requirements of Subsections B.1.a and B.1.b, ROC emissions may be controlled by an emission capture and control system.

- d. ROC containing materials in a solvent flow are applied only as a continuous unbroken stream and not as a dispersed, fine, atomized, or shower type spray, and the method of application shall prevent liquid losses through splashing.
  - e. Liquid solvent leaks of 3 drops per minute or more are repaired within 24 hours of detection or the equipment is shut down until replaced or repaired.
2. No person shall use ROC containing materials for a solvent cleaning operation outside a solvent cleaning station unless:
- a. The solvent composite vapor pressure is 33 mm Hg (0.64 psia) or lower at 20°C (68°F) and the solvent ROC content is equal to or less than the following limits:

LIMITS  
Grams per Liter (g/l) of Solvent

Surface Preparation	450
Repair and Maintenance Cleaning	750
Photoresist Application Equipment Cleaning	950
Other, not listed	200

- b. One of the following cleaning devices or methods is used:
  - 1) Wipe cleaning; or
  - 2) Remote reservoir cold cleaner; or
  - 3) Spray bottles or containers with a maximum capacity of 16 fluid ounces from which solvents are applied without propellant-induced force; or
  - 4) Cleaning equipment utilizing a closable solvent container. The solvent container shall remain closed at all times except while objects to be cleaned are being deposited or removed or when maintenance or repair is being performed on the cleaning equipment.
    - a) If a solvent flow method is used, the solvent shall not be atomized.
    - b) If a solvent flushing method is used, the solvent shall be flushed through the system by pumping.

3. No person, with total combined ROC emissions from photoresist maskant and photoresist developer equal to or greater than 27.22 kilograms (60 pounds) in any month on a facility-wide basis, shall perform photoresist operations at a semiconductor manufacturing facility unless all ROC containing vapors from photoresist operations and solvent cleaning stations are vented to an emission capture and control system.
4. An emission capture and control system, which reduces ROC emissions to the atmosphere, shall:
  - a. Operate at all times the associated equipment is operating.
  - b. Have a combined efficiency of at least 90 percent, by weight.
  - c. Have a collection system which vents all exhaust from photoresist operations and/or cleaning station exhaust to the control device and have one or more inlets for the collection of fugitive emissions.
  - d. Have a continuous monitor which shall:
    - 1) Measure and record applicable key operating parameters such as:
      - a) Destruction device combustion temperature.
      - b) Temperature rise across a catalytic incinerator.
      - c) ROC concentration of a carbon absorption unit to determine breakthrough.
    - 2) Be calibrated according to the manufacturer's specifications.
    - 3) Operate at all times the associated control equipment is operating.
  - e. Receive written approval for such equipment from the Air Pollution Control Officer (APCO) pursuant to Rule 10 of these rules.
5. ROC materials shall be stored in nonabsorbent, nonleaking containers, which shall be kept closed except when adding or removing material.
6. ROC material wastes shall be disposed of in a manner consistent with Federal, State, and local hazardous waste regulations.
7. The manufacturer or supplier of any maskant, developer, which contains ROC, or solvent subject to this rule shall ensure the following information is included on the product container or a data sheet supplied with the product:

- a. Material name, manufacturer identification, specific mixing instructions, and ROC content as applied.
- b. The ROC content of maskants and developer expressed as grams of ROC per liter of maskant or developer, excluding water and exempt compounds.
- c. The ROC content of solvents expressed as grams of ROC per liter of solvent and the composite partial vapor pressure.

C. Recordkeeping Requirements.

Recordkeeping is required only for those maskants, developers, and solvents containing ROC. Any person subject to this rule shall:

1. Maintain a current file for each maskant and developer in use and in storage. The file shall include a data sheet or material list giving the material name, manufacturer identification, specific mixing instructions, and ROC content, as applied.
2. Maintain a current file for each solvent in use and in storage. The file shall include a data sheet or material list giving the material name, manufacturer identification, ROC content and composite partial vapor pressure.
3. If total facility-wide ROC emissions from photoresist maskant and photoresist developer are less than 27.22 kilograms (60 pounds) per month and the requirements of Subsection B.1 are met, maintain records on a monthly basis showing the type and amount of maskant, developer, and solvent used. Like materials may be grouped and the highest ROC content and the minimum density for each like material used or each maskant, developer, and solvent may be itemized and the specific ROC content and density value for each used. Records shall be maintained using one of the following options.
  - a. Develop a detailed record of the amount of maskant, developer, and cleaning station solvent used for each process and report based on throughput for each process. Solvents used outside a solvent cleaning station may be grouped or each may be reported separately.
  - b. Develop a detailed record of the amount of each maskant, developer, and solvent used.
4. If compliance is achieved through use of air pollution control equipment:
  - a. Maintain daily records of key system operating parameters for emission capture and control equipment as specified in the permit to operate.

- b. Maintain records on a monthly basis showing the type and amount of each maskant, developer, and solvent used.
5. Retain inventory, usage records, and emission capture and control equipment operating records for a minimum of two years from the date of each entry and make these records available to the APCO upon request.

D. Test Methods

1. The ROC content of maskants and solvents shall be determined using EPA Reference Method 24 and ARB Method 432 for determination of exempt compounds as necessary.
2. The composite vapor pressure of organic compounds in liquid cleaning materials shall be determined by quantifying the amount of each organic compound in the blend using gas chromatographic analysis (ASTM E260-91) or by using product formulation data and by summing the partial pressures of each compound at 20°C. For the purpose of this calculation, Raoult's Law applies to the blend. The vapor pressure of each single component compound may be determined from ASTM Method D2879-86 or may be obtained from a published source approved by the APCO such as the sources referenced in 40 CFR 52.741.
3. ROC emissions, as specified in Subsection B.4, shall be measured as prescribed by EPA Reference Method 25, for determining total organic emissions, and EPA Reference Method 18, for quantifying emissions of exempt compounds.
4. The capture and control efficiency of air pollution control equipment, as specified in Subsection B.4, shall be determined using applicable methods in 40 CFR 52.741.

E. Violations

1. Failure to comply with any provision of this rule shall constitute a violation of this rule.
2. Any person subject to the provisions of Subsection B.1.b.1) shall comply with the requirements of Subsection B.1.b.2) if total facility ROC emissions are equal to or greater than 40.82 kilograms (90 pounds) in any month.
3. Any person exempt from the provisions of Subsection B.3 shall comply with the requirements of Subsection B.3 if total combined ROC emissions from photoresist maskant and photoresist developer are equal to or greater than 27.22 kilograms (60 pounds) in any month on a facility-wide basis.

F. Definitions

For the purpose of this rule, the following definitions shall apply:

1. "Breakthrough": The point at which the retentive capacity of the adsorption material is reached and the vapor content of the exit air exceeds a predetermined level.
2. "Coating": A thin layer of material applied to a substrate in a relatively unbroken film.
3. "Composite Partial Vapor Pressure": The sum of the partial pressures of the compounds defined as ROC.
4. "Exempt Organic Compounds": As defined in Rule 2 of these rules.
5. "Freeboard Height": The distance from the top of the solvent or solvent overflow drain to the top of the sink or reservoir.
6. "Freeboard Ratio": The freeboard height divided by the smaller of the length or width of the sink or reservoir.
7. "Fugitive Emissions": Uncollected ROC emissions from any portion of the semiconductor manufacturing operation.
8. "Grams of ROC per Liter of Maskant, Excluding Water and Exempt Compounds": The weight of ROC that are emitted during use per combined volume of ROC and maskant solids and can be calculated by the following equation:

$$\text{Grams of ROC per Liter of Maskant, Less Water and Less Exempt Compounds} = \frac{W_s - W_w - W_{es}}{V_m - V_w - V_{es}}$$

Where:	$W_s$	=	weight of reactive compounds that are emitted in grams
	$W_w$	=	weight of water in grams
	$W_{es}$	=	weight of exempt compounds in grams
	$V_m$	=	volume of material in liters
	$V_w$	=	volume of water in liters
	$V_{es}$	=	volume of exempt compounds in liters

9. "Grams of ROC per Liter of Solvent": The weight of ROC per volume of solvent can be calculated by the following equation:

$$\text{Grams of ROC per liter of solvent} = \frac{W_s - W_w - W_{es}}{V_m}$$

Where:  $W_s$  = Weight of reactive compounds in grams  
 $W_w$  = Weight of water in grams  
 $W_{es}$  = Weight of exempt compounds in grams  
 $V_m$  = Volume of material in liters

10. "Photoresist Maskant, Maskant, or Photoresist": A coating applied directly to a component to protect surface areas when chemical milling, etching, or other chemical surface operations are performed on the component.
11. "Photoresist Operation": A process for the application and development of photoresist masking solution on a substrate, including preparation (except primary cleaning), soft bake, develop, hard bake, and stripping of the unhardened or softened photoresist.
12. "Reactive Organic Compounds (ROC)": As defined in Rule 2 of these rules.
13. "Remote Reservoir Cold Cleaner": A device in which solvent is pumped through a sink-like work area for cleaning parts and drains immediately, without forming a pool, through a single drain hole less than 100 square centimeters (15.5 square inches) in area into an enclosed container which is not accessible for soaking parts.
14. "Repair and Maintenance Cleaning": Cleaning of equipment, equipment parts tools, or general work areas as part of a repair operation or as part of a scheduled maintenance procedure during which power to the equipment has been secured.
15. "ROC Materials": Maskants, materials used for cleanup or maskant removal, solvent, paper and cloth, and waste containing, impregnated with, coated with, or mixed with Reactive Organic Compounds.
16. "Semiconductor Manufacture": Any process or operation producing semiconductor material, slicing or polishing semiconductor material, utilizing photoresist to manufacture intermediate products, or producing either semiconductor devices or related solid state devices.
17. "Solvent Cleaning Operation": A cleaning operation utilizing a ROC material and conducted outside a solvent cleaning station for the removal of loosely held uncured maskants and contaminants which include, but are not limited to, dirt, soil, and grease from parts, tools, machinery, equipment, and general work areas. Each distinct method of cleaning in a cleaning process which consists of a series of cleaning methods shall constitute a separate solvent cleaning operation.
18. "Solvent Cleaning Station": A workplace, which is enclosed on three sides and equipped with a vent hood, used to remove surface contaminants, oxide stencil, or

photoresist from the semiconductor substrate using a liquid or vapor solvent containing reactive organic compounds.

19. "Solvent Flushing": The use of a solvent to remove uncured maskants or contaminants from the internal surfaces and passages of the equipment by flushing solvent through the equipment.
20. "Stripping": The removal of spent photoresist maskant from the product after etching, or the removal of oxide stencil from the product after diffusion.
21. "Surface Preparation": The removal of contaminants such as cured maskants, dust, soil, oil, grease, etc., prior to coating applications.
22. "Wipe Cleaning": The method of cleaning which utilizes a material such as a rag dampened, not saturated, with a solvent, coupled with a physical rubbing process to remove contaminants from surfaces.