

RULE 4661 ORGANIC SOLVENTS (Adopted May 21, 1992; Amended December 17, 1992; Amended December 9, 1999; Amended December 20, 2001; Amended May 16, 2002; Amended September 20, 2007).

1.0 Purpose

The purpose of this rule is to limit the emissions of volatile organic compounds (VOCs) from the use of organic solvents. This rule also specifies the reduction, monitoring, reporting, and disposal requirements.

2.0 Applicability

The provisions of this rule shall apply to any source operation that uses organic solvents unless the source operation is exempted under Section 4.0.

3.0 Definitions

3.1 APCO: as defined in Rule 1020 (Definitions).

3.2 ARB: California Air Resources Board.

3.3 Baked: a process whereby the coated object is heated above ambient temperature to a temperature at or above 194°F for the purpose of curing or drying.

3.4 Dissolver: an organic solvent that is added to an adhesive, coating, or ink in order to melt or to liquefy solid particles.

3.5 EPA: United States Environmental Protection Agency.

3.6 Exempt Compounds: all organic compounds not classified as VOC, as listed in the definition of VOC in Rule 1020 (Definitions).

3.7 Grams of VOC per liter of Material: the weight of VOC per volume of material and is calculated by the following equation:

$$\text{Grams of VOC per liter of material} = \frac{W_s - W_w - W_{ec}}{V_m}$$

Where:

W_s = Weight of volatile compounds, in grams

W_w = Weight of water, in grams

W_{ec} = Weight of exempt compounds, in grams

V_m = Volume of material, in liters.

- 3.8 Heat-Cured or Heat-Polymerized: heated to a temperature less than or equal to 194°F for the purpose of curing a coating, ink or adhesive.
- 3.9 Normal Business Hours: Monday through Friday, 8:00 am to 5:00 pm.
- 3.10 Organic Solvent: the same as “Solvent.”
- 3.11 Organic Solvent Cleaning: as defined in Rule 4663 (Organic Solvent Cleaning, Storage, and Disposal).
- 3.12 Photochemically Reactive Solvent: any organic solvent with an aggregate of more than 20% of its total volume composed of chemical compounds classified below or which exceeds any of the following individual percentage composition limitations referring to the total volume of solvent:
- 3.12.1 A combination of hydrocarbons, alcohols, aldehydes, esters, ethers or ketones having an olefinic or cycloolefinic type of unsaturation: five (5) percent; or
 - 3.12.2 A combination of aromatic compounds with eight (8) or more carbon atoms to the molecule except ethylbenzene: eight (8) percent; or
 - 3.12.3 A combination of ethylbenzene, ketones having branched hydrocarbon structures, or toluene: 20%.
- Whenever any organic solvent or any constituent of an organic solvent may be classified from its chemical structure into more than one (1) of the above groups of organic compounds, it shall be considered as a member of the most reactive chemical group, that is, that group having the least allowable percentage of the total volume of solvents.
- 3.13 SCAQMD: South Coast Air Quality Management District.
- 3.14 Solvent: as defined in Rule 4663 (Organic Solvent Cleaning, Storage, and Disposal).
- 3.15 Standard Conditions: as defined in Rule 1020 (Definitions).
- 3.16 Thinner or Viscosity Reducer: an organic solvent which is used to dilute coatings to reduce viscosity, color strength, and solids, or to modify drying conditions.
- 3.17 Volatile Organic Compound (VOC): as defined in Rule 1020 (Definitions).

4.0 Exemptions

The provisions of this rule shall not apply to:

- 4.1 The manufacture of organic solvents, or the transport of organic solvents or materials containing organic solvents.
- 4.2 Any source operation that is subject to or specifically exempted by any of the following rules:
 - 4.2.1 Rule 4601 (Architectural Coatings),
 - 4.2.2 Until December 31, 2008, Rule 4602 (Motor Vehicle and Mobile Equipment Coating Operations),
 - 4.2.3 Rule 4603 (Surface Coating of Metal Parts and Products),
 - 4.2.4 Rule 4604 (Can and Coil Coating Operations),
 - 4.2.5 Rule 4605 (Aerospace Assembly and Component Coating Operations),
 - 4.2.6 Rule 4606 (Wood Products Coating Operations),
 - 4.2.7 Rule 4607 (Graphic Arts),
 - 4.2.8 Rule 4610 (Glass Coating Operations),
 - 4.2.9 On and after January 1, 2009, Rule 4612 (Motor Vehicle and Mobile Equipment Coating Operations – Phase II),
 - 4.2.10 Rule 4653 (Adhesives),
 - 4.2.11 Rule 4662 (Organic Solvent Degreasing Operations),
 - 4.2.12 Rule 4684 (Polyester Resin Operations), or
 - 4.2.13 Rule 4691 (Vegetable Oil Processing Operations).
- 4.3 The spraying or other employment of insecticides, pesticides or herbicides.
- 4.4 The employment, application, evaporation, or drying of saturated halogenated hydrocarbons or perchloroethylene.

- 4.5 The use of any material, in any source operation described in Sections 5.1, 5.2, 5.3, or 5.4 if all of the following conditions are met:
 - 4.5.1 The volatile content of material consists only of water and organic solvents, and
 - 4.5.2 The organic solvents content comprises not more than 20 percent by volume of the total volatile content, and
 - 4.5.3 The volatile content is not photochemically reactive, and
 - 4.5.4 The organic solvent does not come into contact with flame.

5.0 Requirements

- 5.1 Sections 5.2 through 5.7 shall remain in effect until March 20, 2008.
- 5.2 Solvents Subjected to Heat: An operator shall not discharge into the atmosphere more than 15 pounds of VOC emissions in any one (1) day from any source operation in which any organic solvent or any material containing organic solvents comes into contact with a flame or is baked, heat-cured, or heat-polymerized in the presence of oxygen, unless the VOC emissions have been reduced through the operation of an APCO-approved VOC emissions control system with an overall capture and control efficiency of at least 85 percent by weight. Those portions of any series of source operation designed for processing continuous web, strip, or wire that emit VOCs in the course of using operations described in this section shall be collectively subject to compliance with this section.
- 5.3 Photochemically Reactive Solvents: An operator shall not discharge into the atmosphere more than 40 pounds of VOC emissions in any one (1) day from any source operation resulting from conditions other than those described in Section 5.1 for employing or applying any photochemically reactive solvent, or any material containing such photochemically reactive solvent, unless the VOC emissions have been reduced through the operation of an APCO-approved VOC emissions control system with an overall capture and control efficiency of at least 85 percent by weight. Emissions resulting from baking, heat-curing, or heat-polymerizing, as described in Section 5.2 of this rule, shall be excluded from determination of compliance with this section. Those portions of any series of source operation designed for processing a continuous web, strip, or wire that emit VOCs in the course of using operations described in this section shall be collectively subject to compliance with this section.
- 5.4 Non-photochemically Reactive Solvents: An operator shall not discharge into the atmosphere more than 3,000 pounds of VOC emissions in any one (1) day

from any source operation in which any non-photochemically reactive organic solvent or any material containing such a solvent, is employed or applied, unless VOC emissions have been reduced through the operation of an APCO-approved VOC emissions control system with an overall capture and control efficiency of at least 85 percent by weight. Emissions resulting from baking, heat-curing, or heat-polymerizing, as described in Section 5.2 of this rule, shall be excluded from determination of compliance with this section. Those portions of any series of source operation designed for processing a continuous web, strip, or wire that emit VOCs in the course of using operations described in this section shall be collectively subject to compliance with this section.

- 5.5 Cleanup: Emissions of VOCs into the atmosphere resulting from cleanup operations utilizing photochemically reactive organic solvents, from any source operation described in Sections 5.2, 5.3, or 5.4 shall be included with other emissions of VOCs from that source operation for determining compliance with this rule.
- 5.6 Post Removal Drying: Emissions of VOCs into the atmosphere as a result of spontaneously continuing drying of products for the first 12 hours after their removal from any source operation described in Sections 5.2, 5.3, or 5.4 shall be included with other emissions of VOCs from that source operation for determining compliance with this rule.
- 5.7 Monitoring: An operator incinerating, adsorbing, or otherwise processing organic solvents pursuant to this rule shall provide, properly install and maintain in calibration, in good working order and in operation, devices as specified in the Authority to Construct or the Permit to Operate, or as specified by the APCO, for indicating temperatures, pressures, rates of flow or other operating conditions necessary to determine the degree and effectiveness of the VOC emission control system.
- 5.8 On and after March 21, 2008, from all VOC-containing materials, equipment, and processes subject to this rule, an operator shall not emit to the atmosphere VOCs in excess of 833 pounds VOC per calendar month per facility.
- 5.9 In lieu of meeting the VOC emission limit in Section 5.8, an operator may install and operate a VOC emission control system that meets the following requirements.
 - 5.9.1 The VOC emission control system shall be approved by the APCO.
 - 5.9.2 The VOC emission control system shall have a capture efficiency of at least 90 percent by weight (90 wt%) and a control efficiency of at least 95 wt%.

5.10 Organic Solvent Cleaning, Storage, and Disposal Requirements

Operators shall comply with the requirements of Rule 4663 (Organic Solvent Cleaning, Storage, and Disposal) when performing organic solvent cleaning, storage and disposal of organic solvents and waste solvent materials, coatings, adhesives, catalysts, and thinners. See Sections 5.0 and 6.0 of Rule 4663 for solvent VOC content limits, work practices, recordkeeping, and testing requirements.

6.0 Administrative Requirements

6.1 Recordkeeping

6.1.1 Until March 20, 2008, the records shall identify the organic solvents used in all source operations and shall include the name of each organic solvent, solvent manufacturer's name, chemical composition, VOC content, vapor pressure, amount used.

6.1.1.1 An operator of a coating operation subject to this rule shall maintain daily records.

6.1.1.2 For other operations subject to this rule, records may be kept on an extended basis, but not to exceed monthly, and shall not exceed a period during which the amount of VOC emissions exceeds the applicable daily VOC emission limits in the rule.

6.1.1.3 Solvent purchase records and other such records needed to verify compliance of emissions limits of the rule shall also be kept.

6.1.1.4 Other such records, including the amount of VOC emissions resulting from organic solvent cleaning operations subject to Rule 4663 utilizing photochemically reactive organic solvents, needed to verify compliance of emissions limits of the rule shall also be kept.

6.1.2 On and after March 21, 2008, operators shall

6.1.2.1 Materials List: An operator shall maintain and have available on site, a current list of materials in use which provides all of the data necessary to evaluate compliance including the following information as applicable:

6.1.2.1.1 Specific manufacturer's name of solvent-containing material, including solvents, catalysts, and thinners.

6.1.2.1.2 VOC content of each solvent-containing material, as used, in g/l or lb/gal.

6.1.2.2 Material Usage Records – An operator shall maintain usage records on a daily basis that include the following information:

6.1.2.2.1 Specific material.

6.1.2.2.2 Volume of material used (gallons).

6.1.2.2.3 Specific solvents, catalysts and thinners added to material.

6.1.2.2.4 Volume of each solvent, catalyst and thinner (gallons) added.

6.1.2.2.5 When the material is a mixture of different materials that are blended by the operator, the mix ratio of the batch shall be recorded and the VOC content of the batch shall be calculated and recorded in order to determine compliance with the VOC emission limits.

6.1.3 VOC Emission Control System Records

An operator using a VOC emission control system as a means of complying with this rule shall maintain daily records of key system operating parameters which will demonstrate continuous operation and compliance of the VOC emission control system during periods of emission-producing activities.

6.1.4 Records Retention

An operator shall retain records required in Sections 6.1.1 through 6.1.3, as applicable, on site for a minimum of five (5) years, make the records available on site during normal business hours to the APCO, ARB, or EPA and submit the records to the APCO, ARB, or EPA upon request.

6.2 Test Methods

6.2.1 Determination of VOC Content

6.2.1.1 The VOC content of organic solvents shall be determined by using EPA Test Method 24 or 24A or by using the manufacturer's product formulation data and the formula in Section 3.7.

6.2.1.2 Exempt halogenated VOCs shall be determined by using the ARB Test Method 432 or SCAQMD Test Method 303.

6.2.2 Determination of Overall Capture and Control Efficiency of VOC Emission Control Devices

6.2.2.1 The capture efficiency of a VOC emission control system's collection device(s) shall be determined according to EPA's "Guidelines for Determining Capture Efficiency," January 9, 1995 and 40 CFR 51, Appendix M, Test Methods 204-204F, as applicable, or any other method approved by EPA, ARB, and the APCO.

6.2.2.2 The control efficiency of the VOC emission control system's control device shall be determined by using EPA Methods 2, 2A, or 2D for measuring flow rates and EPA Method 25, 25A, or 25B for measuring total gaseous organic concentrations at the inlet and outlet of the control device. EPA Method 18 or ARB Method 422 shall be used to determine the emissions of exempt compounds. The control efficiency of the VOC emission control system's control device shall be calculated by using the following equation:

$$CE_{\text{CONTROL}} = [1 - (\text{VOC}_{\text{OUT}} / \text{VOC}_{\text{IN}})] \times 100\%$$

Where:

CE_{CONTROL} = Control Efficiency, in percent

VOC_{IN} = VOC content, in grams/liter, less exempt compounds and water, into the control device

VOC_{OUT} = VOC content, in grams/liter, less exempt compounds and water, out of the control device.

6.2.2.3 For VOC emission control systems that consist of a single VOC emission collection device connected to a single VOC emission control device, the overall capture and control efficiency shall be calculated by using the following equation:

$$CE_{\text{CAPTURE \& CONTROL}} = [CE_{\text{CAPTURE}} \times CE_{\text{CONTROL}}] / 100 \%$$

Where:

$CE_{\text{CAPTURE \& CONTROL}}$ = Overall Capture and Control Efficiency, in percent

CE_{CAPTURE} = Capture Efficiency of the collection device, in percent, as determined in Section 6.2.2.1

CE_{CONTROL} = Control Efficiency of the control device, in percent, as determined in Section 6.2.2.2.

6.2.3 Determination of VOC Emissions

6.2.3.1 The emissions of VOCs, measured and calculated as carbon, shall be determined by using EPA Test Method 25, 25A, or 25B, as applicable. EPA Test Method 18 or ARB Method 422 shall be used to determine the emissions of exempt compounds.

6.2.3.2 Total VOC emissions per day shall be determined for each source operation by using the following equation:

$$E_{\text{Total}} = \left[\left(\sum_{i=1}^k L_i V_i \right) + \left(\sum_{m=1}^n L_m V_m \times (1 - CE / 100\%) \right) \right] / 454$$

Where:

E_{Total} = Total VOC emissions, in pounds per day

L_i = Liters per day used of the “i”th organic solvent that is uncontrolled

V_i = Grams of VOC per liter of material of the “i”th organic solvent that is uncontrolled

L_m = Liters per day used of the “m”th organic solvent that is controlled

V_m = Grams of VOC per liter of material of the “m”th organic solvent that is controlled

CE = Overall capture and control efficiency of the control device, in percent, as determined in Section 6.2.2.3.

6.2.4 Multiple Methods of Determination

VOC emissions and overall capture and control efficiency determined to exceed any limits established by this rule through the use of any of the above-referenced test methods and equations shall constitute a violation of the rule.