

Air Pollution Control Board
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Air Pollution Control Officer R. J. Sommerville

December 8, 1992

TO:

Rule 67.12 - Polyester Resin Operations

Workshop Participants and Other Interested Parties

FROM:

Richard J. Smith

**Deputy Director** 

# RULE 67. 12 - FINAL RULE AND WORKSHOP REPORT

Attached for your review are the workshop report and the final draft of amended Rule 67.12 that will be considered for adoption by the Air Pollution Control Board. Also, attached are suggested recordkeeping forms that can be used as guidelines in developing recordkeeping procedures. The rule will likely be scheduled for public hearing in February 1993.

If you have any questions, please call Natalie Zlotin (619) 694-3312 or me at (619) 694-3303.

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**Deputy Director** 

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# RULE 67.12 POLYESTER RESIN OPERATIONS

## WORKSHOP REPORT

A workshop notice was mailed to each company known to be involved in Polyester Resin Operations in San Diego County. Notices were also mailed to all Economic Development Corporations and Chambers of Commerce in San Diego County, polyester resin manufacturers, the U.S. Environmental Protection Agency (EPA), the California Air Resources Board (ARB), and other interested parties.

The workshop was held on November 5, 1992, and was attended by fourteen people. Written comments were also received. The comments and District responses are as follows:

# **WORKSHOP COMMENT:**

Why was the exemption for coatings subject to Rule 67.3 or Rule 67.0 added to Section (b)?

# **DISTRICT RESPONSE:**

This exemption was added to avoid having a coating operation being regulated by two or more different rules. For example, there are cases were polyester resin material may be applied to a metal part substrate. Without the exemption in Section (b), it would be regulated by both Rule 67.3 and Rule 67.12. Regulation by two rules was not intended. In addition, the District will add an exemption to Section (b) for coating operations subject to Rule 67.11 - Wood Products Coating Operations.

#### **WORKSHOP COMMENT:**

Why are daily records required for claiming the exemptions while the recordkeeping requirement in Subsection (f)(3) is on a monthly basis?

#### **DISTRICT RESPONSE:**

Recordkeeping on a monthly basis is sufficient when a facility uses compliant polyester resin materials. However, the exemption limits in Subsections (b)(1) and (b)(2) are based on daily usage. Therefore, daily records are required to verify the exemption criteria are met on a daily basis.

# **WORKSHOP COMMENT:**

Does "cleaning materials" refer to materials containing volatile organic compounds (VOC)? If so, this should be specifically stated.

# **DISTRICT RESPONSE:**

Yes, "cleaning material" refers to VOC-containing materials. The definition has been modified to clarify this.

### **WORKSHOP COMMENT:**

What was the reason for the addition of "acute or chronic exposure to corrosive, caustic and/or acidic agents" to the language of the definition of "corrosion resistant resin"?

#### **DISTRICT RESPONSE:**

This language was added to clarify the definition. This added language is consistent with the statewide Reasonable Available Control Technology/Best Available Retrofit Control Technology (RACT/BARCT) determination recommended by the ARB.

#### **WORKSHOP COMMENT:**

The terms "acute or chronic exposure" used in the definition of "corrosion resistant resin" are more applicable to human exposures. Perhaps "limited and prolonged" would be more suitable.

# **DISTRICT RESPONSE:**

The District agrees and has modified the definition of "corrosion resistant resin" accordingly.

# **WORKSHOP COMMENT:**

Are gel coats with monomer content limits specified in Subsection (d)(1)(ii) available?

# **DISTRICT RESPONSE:**

Information provided to the District indicates that gel coats with monomer contents that comply with the limits of Subsection (d)(1)(ii) are currently available and are already in use by facilities in San Diego County.

# **WORKSHOP COMMENT:**

The proposed rule allows for cleaning materials with initial boiling points greater than 190°C to be used. Is there any intent to indicate a vapor pressure equivalency? What chemicals did the District have in mind and are they effective cleaners?

# **DISTRICT RESPONSE:**

The District does not intend to provide a vapor pressure equivalency since it is not simple to establish a direct relation between initial boiling point and the vapor pressures of solvents, especially solvent mixtures. The District has opted to include initial boiling point criteria rather than vapor pressure because there are ASTM test methods approved by EPA and ARB for initial boiling point of organic compounds.

Dibasic ester is one solvent that meets these criteria. The information provided to the District indicates this is an effective alternative cleaning material with an initial boiling point greater than 190°C.

### **WORKSHOP COMMENT:**

Does acetone fall under the category of cleaning materials in Subsection (d)(1)(vi)(A) that contain less than 200 grams of VOC per liter?

#### **DISTRICT RESPONSE:**

No. Acetone is an organic solvent. The VOC content of acetone is 792 grams per liter. Therefore, a solvent reclamation system would be required when acetone is used, unless usage is less than 0.5 gallons per day.

#### **WORKSHOP COMMENT:**

If less than 0.5 gallon per day of acetone is used, is the operation exempt from the reclamation system requirement?

#### **DISTRICT RESPONSE:**

Yes, provided that the combined usage of acetone and/or other solvents containing more than 200 grams of VOC per liter or having an initial boiling point less than 190°C is less than 0.5 gallon (average) per operating day. This usage is an average based on the number of operating days and calculated from the monthly usage records.

#### **WORKSHOP COMMENT:**

What does the term "records" mean in Section (f)? Does this refer to usage records only?

#### **DISTRICT RESPONSE:**

"Records" means documentation containing the information specified in Section (f), including but not limited to usage figures. In some instances, such as the requirements of Subsection (f)(1), material safety data sheets (MSDS) and/or manufacturer specifications for material application are sufficient. When a facility intends for MSDS's or manufacturer's specifications to be the "records" used to comply with Subsection (f)(1), these should be specific to the materials reported as being used in that operation and not a collection of MSDS's and manufacturer specifications for all materials found in the facility.

## **WORKSHOP COMMENT:**

Will separate records have to be kept on information already on MSDS's or are MSDS's adequate?

#### **DISTRICT RESPONSE:**

MSDS's are typically adequate.

#### **WORKSHOP COMMENT:**

Must everything required in Subsection (f)(1) be recorded each time there is an entry of usage?

### **DISTRICT RESPONSE:**

No. Subsection (f)(3) requires monthly records of the usage of polyester resin material and cleaning materials. Subsection (f)(1) requires that for every product used, according to the monthly records, there be records available containing the information required in (f)(1). One set of records with the data required in Subsection (f)(1) is sufficient provided it includes of every product used in a polyester resin operation.

#### **WORKSHOP COMMENT:**

Must the VOC content of thinners also be recorded and how should usage be recorded?

#### **DISTRICT RESPONSE:**

Yes, records of the VOC content of thinners should be maintained. Usage can be recorded as a mix ratio of the resins used.

#### **WORKSHOP COMMENT:**

A model record sheet may help facilities to understand the recordkeeping requirements and more easily comply.

### **DISTRICT RESPONSE:**

The District is currently working on developing a model record sheet and will make it available to affected businesses.

#### **WORKSHOP COMMENT:**

Can Subsections (f)(1) and (f)(2) be combined?

### **DISTRICT RESPONSE:**

Yes, Subsections (f)(1) and (f)(2) have been combined.

#### **WORKSHOP COMMENT:**

If an operation currently has a permit to operate with a condition to maintain daily records, does this condition still hold despite the new monthly recordkeeping requirements proposed?

#### **DISTRICT RESPONSE:**

A daily recordkeeping condition in a permit to operate will still be applicable if the condition was included for any reason other than Rule 67.12 requirements. For example, if daily recordkeeping was included for New Source Review purposes, the condition will remain and be enforced. Daily recordkeeping conditions that are included solely because of Rule 67.12 requirements will need to be modified. When the proposed revisions to Rule 67.12 are adopted, the District will send an Advisory to all affected facilities. The Advisory will discuss how permit conditions will be changed to reflect

the new recordkeeping provisions. Until this is done, facilities with permits stipulating daily record-keeping are advised not to make changes to recordkeeping frequency.

# **WORKSHOP COMMENT:**

Must a facility that has expended time and money in developing daily recordkeeping procedures now switch to monthly recordings?

# **DISTRICT RESPONSE:**

No. If a facility has daily recordkeeping procedures in effect and does not wish to make the transition to monthly records, it has that option. The purpose of changing to monthly records is to reduce the burden of maintaining records. If it would be more burdensome for a facility to change to monthly records, the facility may continue with daily records. Subsection (f)(3) has been modified to allow for daily recordkeeping.

After the proposed revisions to Rule 67.12 have been adopted, a facility should verify that all of the information requested in the revised rule is being recorded.

## **WORKSHOP COMMENT:**

Is SCAQMD Method 312-91 that is specified in Subsection (g)(1) a lengthy calculation?

# **DISTRICT RESPONSE:**

SCAQMD Method 312-91 is not a calculation, but a test method to measure the monomer content of resins. Test methods are not required to be performed by a facility. Test methods will be used by regulatory agencies, such as the District, ARB or EPA, for compliance verification purposes. Manufacturers are also encouraged to use test methods specified in Rule 67.12 for the data they provide in MSDS's. However, if facilities desire to do so, they can use these same test methods to evaluate their own compliance status.

#### **WORKSHOP COMMENT:**

Can a facility get a copy of SCAQMD Method 309-91? Is it simple enough for a shop to run?

# **DISTRICT RESPONSE:**

A facility interested in obtaining a copy of this test method may contact the District's Rule Development Section directly. However, these tests are intended for testing laboratories properly equipped to perform them. If a shop has the equipment required to run the test, it could do so to verify they are in compliance.

# **EPA COMMENT:**

SCAQMD Test Methods 309-91 and 312-91, and ARB Test Method 401 specified in Section (g) have not been approved by EPA.

# **DISTRICT RESPONSE:**

These test methods are currently being reviewed by EPA headquarters. There are no EPA approved methods that may be used in lieu of those cited in Rule 67.12.

# **ARB COMMENT:**

Subsection (g)(2) cites SCAQMD Test Method 309-91 for determination of "weight loss". This should read "weight loss per square meter".

#### **DISTRICT RESPONSE:**

The District agrees. This subsection has been modified as suggested.

# **ARB COMMENT:**

Subsection (g)(6) should read "...only if the presence of such compounds..." to clarify that perfluorocarbons will be assumed to be absent if the material manufacturer does not fulfill the requirements stipulated in this subsection.

# **DISTRICT RESPONSE:**

The District agrees. This subsection has been modified as suggested.

RS:jo 11/17/92

# AIR POLLUTION CONTROL DISTRICT COUNTY OF SAN DIEGO

#### PROPOSED AMENDMENTS TO RULE 67.12

#### RULE 67.12. POLYESTER RESIN OPERATIONS

## (a) APPLICABILITY

Except as otherwise provided in Section (b), this rule is applicable to polyester resin operations.

Polyester resin operations subject to this rule shall not be subject to Rule 66.

#### (b) EXEMPTIONS

- (1) Except for marine vessel repair operations, the provisions of this rule shall not apply to any polyester resin operations where the combined consumption of polyester resins, including corrosion resistant resin, fire retardant resin, gel coat, and eleanup solvent cleaning materials is less than 1 gallon for each operating day.
- (2) The provisions of this rule shall not apply to any marine vessel repair operation using polyester resin materials where the combined consumption of polyester resins, including corrosion resistant resin, fire retardant resin, gel coat, and eleanup solvent cleaning materials is less than 0.5 gallon for each operating day.

It shall be the responsibility of any person claiming either of the above exemptions specified in Subsections (b)(1) or (b)(2) to maintain daily records necessary for the District to determine the applicability of such an exemption. The records shall be maintained on site for at least three years and shall be n ade available to the District immediately upon request.

(3) The provisions of this rule shall not apply to coatings subject to Rules 67.3, or 67.0 or 67.11.

## (c) **DEFINITIONS**

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

- (1) "Catalyst" means a substance added to the resin to accelerate the rate of curing.
- (2) "Cleaning Materials" means materials containing volatile organic compounds (VOC's) used for the cleaning of hands, tools, molds and spray equipment associated with polyester resin operation: which contain more than 200 grams of VOC per liter.

- (3) "Closed Mold Operation" means a method of forming objects from polyester resins by placing the material in a confining mold cavity and applying pressure and/or heat.
- (4) "Controlled Enclosure" means a structure having at least three sides and a roof and which is designed to capture process emissions to meet the requirements of all District prohibitory standards (e.g., Rules 50, 51, 52, 71, etc.).
- (5) "Controlled Process" means a modification to a dry sanding, grinding or cutting operation which uses water sprays, vacuum devices or other techniques to control the emission of particulates to the atmosphere to meet the requirements of all District prohibitory standards (e.g., Rules 50, 51, 52, 71, etc.).
- (6) "Corrosion Resistant Resin" means a halogenated, furan, bisphenol A, vinyl ester, or isophthalic resin which is used to make products for acute or chronic exposure to corrosive, caustic and/or acidic agents, corrosive service.
- (7) "Cross-Linking" means the process of joining two or more polymer chains together.
- (8) "Cure" means the polymerization, i.e. the transformation from a liquid to a solid state, to achieve desired product physical properties, including hardness.
- (9) "Exempt Compound" means any of the following compounds or classes of compounds: 1,1,1-trichloroethane, methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), chlorodifluoromethane (HCFC-22), trifluoromethane (HCFC-23), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114), chloropentafluoroethane (CFC-115), dichlorotrifluoroethane (HCFC-123), dichlorofluoroethane (HCFC-141b), tetrafluoroethane (HFC-134 and HFC-134a, both isomers), chlorodifluoroethane (HCFC-142b), chlorotetrafluoroethane (HCFC-124), pentafluoroethane (HFC-125), trifluoroethane (HFC-143a), difluoroethane (HFC-152a); and the following four classes of perfluorocarbon (PFC) compounds:
  - (i) cyclic, branched, or linear, completely fluorinated alkanes:
  - (ii) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
  - (iii) cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and
  - (iv) sulphur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

- (10)(9) "Fiberglass" means a fiber similar in appearance to wool or cotton fiber but made from glass.
- (11)(10) "Fire Retardant Resin" means a resin designed for the purpose of delaying the spread of combustion.
- (12)(11) "Gel Coat" means a polyester resin surface coat, either colored or clear, providing a cosmetic enhancement and improvement to exposure resistance.
- (13)(12) "High-Volume Low-Pressure (HVLP) Spray" means a coating application method using pressurized air at a permanent pressure between 0.1 and 10.0 psig, not to exceed 10.0 psig, measured at the air cap of the coating application system, and a permanent liquid coating pressure of not more than 50 psig.
- (14)(13) "Inhibitor" means a substance designed to slow down or prevent a chemical reaction.
- (15)(14) "Monomer" means an organic compound that combines with itself or other similar compounds by a cross-linking reaction to become a part of a cured thermosetting resin.
- (16)(15) "Polyester" means a complex polymeric ester, derived from difunctional acids and alcohols, which is dissolved in a monomer.
- (17)(16) "Polyester Resin Operation" means any of the following: mixing, pouring, hand lay-up, injection, forming, spraying, and curing of polyester resin materials excluding injection molding.
- (18)(17) "Polyester Resin Materials" means unsaturated polyesters, cross-linking agents, catalysts, gel coats, inhibitors, and any other material containing VOC used in a polyester resin operation.
- (19)(18) "Polymer" means a large chemical chain composed of identical cross-linked groups, such as polystyrene.
- (20)(19) "Reclamation System" means equipment capable of reclaiming spent cleaning materials for reuse. Reclamation may be done onsite or by using an offsite commercial reclamation facility.
- (21)(20) "Repair" means the addition of polyester resin to portions of a previously fabricated product in order to mend mechanical damage which occurs after the normal fabrication process.
- (22)(21) "Resin" means any of a class of organic polymers of natural or synthetic origin used in reinforced products to surround and hold fibers, and is solid or semi-solid in the cured state.
- (23)(22) "Touch-up" means that portion of the polyester resin operation that is necessary to cover minor imperfections.

- (24)(23) "Vapor Suppressed Resin" means a resin which has been modified such that to minimize the weight loss from VOC emissions during polymerization. -does not exceed 60 grams per square meter of exposed area.
- (25) (24) "Volatile Organic Compound (VOC)" means any compound of carbon, which may be emitted to the atmosphere during polyester resin operations, except methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, 1,1,1-trichloroethane, methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), chlorodifluoromethane (CFC-22), trifluoromethane (FC-23), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114), chloro-pentafluroethane (CFC-115), dichlorodifluoroethane (HCFC-123), dichlorofluoroethane (HCFC-141b), tetrafluoroethane (HFC-134a) and chlorodifluoroethane (HCFC-142b) and exempt compounds. For purposes of calculating VOC content of polyester resin material to determine compliance with this rule, any water or any of the above excluded volatile exempt compounds of carbon shall not be considered to be part of the polyester resin material. VOC content of cleaning materials is expressed in grams of VOC per liter of material.
- (26)(25) "Waste Material" means any waste material containing VOC including, but not limited to, any paper or cloth used for cleaning operations, waste resins, and any spent cleaning materials containing VOC.

# (d) STANDARDS

Except as provided for in Subsection (d)(2):

- (1) Any person operating a polyester resin operation <u>subject to this rule where</u> combined consumption of polyester resin material and cleanup material is 10 gallons per day or more shall:
  - (i) Use polyester resin material which contains no more than 35 percent by weight of monomer, as applied and as indicated in the manufacturer's specifications for application, or use a vapor suppressed resin such that the weight loss from VOC emissions does not exceed 60 grams per square meter of exposed surface area during resin polymerization, or use a closed mold system. The provisions of this subsection shall not apply to the use of gel coats, corrosion resistant resins or fire retardant resins; and,
  - (ii) Use gel coats with a monomer content of not more than 45 percent by weight for pigmented gel coats or 50 percent by weight for clear gel coats, as applied and as indicated in the manufacturer's specifications for application; and,

- (iii)(ii) Use a corrosion-resistant or fire retardant resin with a monomer content of no more than 50 percent by weight, as applied and as indicated in the manufacturer's specifications for application; and,
- (iv)(iii) Use self-closing containers for storing, except during the transfer of resin or solvent, all polyester resin, VOC containing cleaning materials and solvent-laden rags, including waste materials; and,
- (v)(iv) Conduct all dry sanding, grinding and cutting operations of polyester resin which contains fiberglass either inside a controlled enclosure or using a controlled process. For marine vessel repair operations this requirement shall apply only for sanding, grinding or cutting operations conducted on the exterior of a vessel hull. This requirement shall not apply to any portable drilling operations; and,
  - (vi)(v) Use a VOC reclamation system for cleaning materials, unless
    - (A) the materials contain less than 200 grams of VOC per liter (1.7 lb/gal);
    - (B) the materials have initial boiling points greater than 190° C (374° F); or
    - (C) the combined usage of materials not complying with (A) or (B) above, is less than 0.5 gallons average per operating day, calculated from monthly records maintained in accordance with Section (f).

-solvents containing more than 200 grams of VOC per liter (1.7 lb/gal). The solvent residue from the reclamation system shall not contain more than 20 percent VOC by weight; and,

- (vii)(vi) Use only airless, air-assisted airless, high-volume low-pressure spray equipment or electrostatic spray equipment for spray operations except for touch-up and repair operations using a hand held air atomized spray gun which has a container for the resin as part of the gun; and,
- (viii)(vii) Not use a polyester resin or cleaning material subject to this rule that, after December 4, 1990, was newly formulated to contain or reformulated to increase the content of, methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114) or chloropentafluoroethane (CFC-115).
- (2) After December 4, 1991, any person operating a polyester resin operation where combined consumption of polyester resin and cleanup material is less than 10 gallons per day shall be subject to the requirements of Subsection (d)(1).
- (2)(3) A person shall not sell or, offer for sale, a polyester resin or cleaning material subject to this rule that, after December 4, 1990, was newly formulated to contain or reformulated to increase the content of, methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114) or chloropentafluoroethane (CFC-115).

or

(3)(4) After December 4, 1990, a A person shall not manufacture, sell, offer for sale, or supply any coating or cleaning materials for use in polyester resin operations unless polyester resin or cleaning material container displays the content of methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114), or chloropentafluoroethane (CFC-115).

#### (e) RESERVED

#### (f) RECORDKEEPING

Any person subject to the requirements of Subsections (d)(1) and (d)(2) of this rule shall maintain records of VOC-containing materials in accordance with the following:

- (1) Maintain a current list records of polyester resin materials and gel coats used, and VOC's in use which provides all of the polyester resin the manufacturer identification, material specifications, monomer contents, and content of any catalysts, fillers, and/or diluents, including thinners, and type of each resin (i.e. regular, vapor-suppressed, corrosion-resistant, or fire retardant) or gel coat (i.e. pigmented or clear). and VOC data necessary to evaluate compliance. (2) For vapor suppressed resins, also maintain records showing manufacturer's information on the weight loss during resin polymerization. , the monomer percentage, and the gel time for each resin.
- (2) Maintain current records of the types of each resin (i.e., regular, vapor-suppressed, corrosion resistant, or fire retardant) and/or gel coat (i.e., pigmented or clear) used.
- (2) (3) Maintain current records of the manufacturer's identification and VOC content of the cleaning materials used.
- (3) (4) Maintain records on a daily or monthly basis showing the type manufacturer's identification and amount of each polyester resin material and cleaning material VOC used.
- (4) (5) Maintain records of the content of methylene chloride, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114) and chloropentafluoroethane (CFC-115) contained in any polyester resin material or cleaning material used.
- (4) Maintain records on a daily basis showing the types and amounts of solvents used for surface preparation and cleanup.

Such records shall be retained on site for at least three years, and shall be made available to the District immediately upon request.

# (g) TEST METHODS

- (1) Measurement of the monomer content of resins subject to Subsections (d)(1)(i), (d)(1)(ii), or (d)(1)(iii) of this rule shall be conducted and reported in accordance with SCAOMD Method 312-91 for determination of percent monomer in polyester resin.
- (2) Measurement of VOCs the polyester resin material weight loss per square meter subject to Subsection (d)(1)(i) of this rule shall be conducted and reported in accordance with SCAOMD Method 309-91 for determination of static volatile emissions. the South Coast Air Quality Management District's "Standard Method for Static Volatile Emissions" as it exists on December 4, 1990 outlined in the "Laboratory Methods of Analysis for Enforcement Samples" Manual.
- (3) Measurement of the VOC content of cleaning materials subject to Subsection (d)(1)(vi)(A) of this rule shall be conducted and reported in accordance with EPA Method 24 (40 CFR 60, Appendix A) as it exists on (date of adoption).
- (4) Measurement of the initial boiling point of cleaning materials subject to Subsection (d)(1)(vi)(B) of this rule shall be conducted and reported in accordance with ASTM test method D1078-86 (Distillation Range of Volatile Organic Liquids).
- (d)(1)(vi)(v) of this rule shall be conducted and reported in accordance with Air Resources Board Method 401 for Determining Solvent Residue, as it exists on December 4, 1990 (date of adoption). and ASTM Standard Practice for Determining VOC Content of Paints and Related Coatings, D3960-87.
- (6) Perfluorocarbon compound(s) shall be recognized as exempt compounds pursuant to Subsection (c)(9) only if the presence of such compounds is claimed by the manufacturer of the material containing the compound, and if the manufacturer identifies a test method for quantifying the identified compounds which has been approved by the Air Pollution Control Officer, the Air Resources Board, and the Environmental Protection Agency.