ATTACHMENT B

15-DAY NOTICE

PROPOSED MODIFIED ARB METHOD 310: Determination of Volatile Organic Compounds (VOC) in Consumer Products

[Note: The text proposed for deletion is shown in **~~bold strikeout~~** and the new text is shown in **bold underline**. Modifications to the originally proposed regulatory language are shown in **bold double-underline** to indicate additions and ***~~bold italic strikeout~~*** to show deletions.]. This revision proposes modifications to ARB Method 310 incorporated by reference in the consumer products regulation.

California Environmental Protection Agency

Air Resources Board

METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS

(Including Appendices A and B)

Adopted: September 25, 1997 **and as last amended on (date)**

DISCLAIMER: Mention of any trade name or commercial product in Method 310 does not constitute endorsement or recommendation of this product by the Air Resources Board.

METHOD 310
DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS

1 APPLICABILITY

1.1 This method (Method 310) applies to the determination of the percent by weight of **(1)** volatile organic compounds (VOC) in consumer products, antiperspirant and deodorant products, and aerosol coatings products **as those terms are defined in Title 17, California Code of Regulations (CCR), Division 3, Chapter 1, Subchapter 8.5 (Consumer Products), commencing with section 94500**, **and (2) low vapor pressure-volatile organic compounds (LVP-VOC) as that term is defined in section 94508(a)(78).** ~~**as defined in Title 17, California Code of Regulations, Sections 94500 et seq.**~~

1.2 Method 310 determines the total volatile material in a product and the presence of any compounds prohibited by ARB regulations ("prohibited compounds"). Components of the product that do not meet the definition of a VOC or are exempted by ARB regulations for a specific product category ("exempt compounds") are subtracted from the total volatile material to determine the final VOC content for the product.

1.3 Method 310 does not apply to the determination of the composition or concentration of fragrance components ~~**or Low Vapor Pressure (LVP) compounds**~~ in products.

1.4 The term "Executive Officer" as used in this document means the Executive Officer of the Air Resources Board or his or her authorized representative.

2 TEST METHODS

Method 310 incorporates by reference the following American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health (NIOSH), and United States Environmental Protection Agency (US EPA) analytical test methods:

2.1 ASTM D 2369-**97** ~~**87**~~: Standard Test Method for Volatile Content of Coatings **(July 10, 1997)** ~~**(June 10, 1987)**~~.

2.2 ASTM D 1426-93: Standard Test Methods for Ammonia Nitrogen in Water (September 15, 1993).

2.3 ASTM D 4017-**96a** ~~**88**~~: Standard Test Method for Water in Paints and Paint Materials by the Karl Fisher Titration Method **(July 10, 1996)** ~~**(October 31, 1988)**~~.

2.4 ASTM D 3792-**91** ~~**86**~~: Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph **(May 15, 1991)** ~~**(November 28, 1986)**~~.

2.5 ASTM D 859-**94** ~~**88**~~: Standard Test Method for Silica in Water (determination of polymethylsiloxanes after digestion) **(May 15, 1994)** ~~**(August 19, 1988)**~~.

2.6 ASTM D 3074-**94** ~~**72**~~: ~~**(Reapproved 1998)**~~ Standard Test Methods for Pressure in Metal Aerosol Containers **(November 15, 1994)** ~~**(Approved July 28, 1972 and reapproved in 1988)**~~ with the modifications found in Appendix A **to this Method 310**.

2.7 ASTM D 3063-**94** ~~**79**~~: ~~**(Reapproved 1988)**~~ Standard Test Methods for Pressure in Glass Aerosol Bottles **(November 15, 1994)** ~~**(April 27, 1979 and reapproved in 1984)**~~ with the modifications found in Appendix A **to this Method 310**.

2.8 ASTM D 3064-89: Standard Terminology Relating to Aerosol Products (November 24, 1989).

2.9 NIOSH: Method 1400 Alcohols I (analysis of acetone and ethanol by gas chromatography). NIOSH Manual of Analytical Methods, Volume 1 (February 1984).

2.10 **Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and~~/or~~ prohibited compounds in the product by headspace/gas chromatography/mass spectrometry)** ~~**US EPA Method 8240, September 1986 revision 0, Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and/or prohibited compounds in the product by headspace/gas chromatography/mass spectrometry), Test Methods for Evaluating Solid Waste, Volume 1 B: Laboratory Manual Physical Chemical Methods, SW-846, November 1986.**~~.~~

2.10.1 US EPA Method 8240B, September 1994, Revision 2, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste, Volume 1 B, Chapter 4, Section 4.3.2: Laboratory Manual Physical/Chemical Methods, SW-846, September 1994.

2.10.2 US EPA Method 8260B, December 1996, Revision 2, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste, Volume 1 B, Chapter 4, Section 4.3.2: Laboratory Manual Physical/Chemical Methods, SW-846, December 1996.

2.11 US EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings: 40 Code of Federal Regulations (CFR) Part 60, Appendix A, as it existed on July 1, 1994.

2.12 US EPA Reference Method 24A, Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.

2.13 US EPA Reference Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.

2.14 US EPA Method 300.7, March, 1986. Dissolved Sodium, Ammonium, Potassium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography.

2.15 ASTM D 86-96: Standard Test Methods for Distillation of Petroleum Products (April 10, 1996).

2.16 ASTM D 850-93: Standard Test Methods for Distillation of Industrial Aromatic Hydrocarbons and Related Materials (April 15, 1993).

2.17 ASTM D 1078-97: Standard Test Methods for Distillation Range of Volatile Liquids (July 10, 1997).

2.18 ASTM D 2879-97: Standard Test Method for Vapor-Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope (April 10, 1997) with the modifications found in Appendix B to this Method 310.

2.19 ASTM D 2887-97: Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (April 10, 1997).

2.20 ASTM E 1719-97: Standard Test Method for Vapor Pressure of Liquids by Ebulliometry (March 10, 1997).

3 TESTING PROCEDURE

3.1 The testing begins when the Executive Officer selects a consumer product sample for analysis by Method 310. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process.

3.2 Initial Testing of Aerosol Products

If the sample is an aerosol product, the aerosol propellant is separated from the liquid portion of the product by using ASTM D 3074-**94** ~~**72**~~ (as modified in Appendix A for metal aerosol container) or ASTM D 3063-**94** ~~**79**~~ (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for exempt or prohibited compounds by using US EPA **Reference** Method 18. The remaining liquid portion of the product is then analyzed as specified in section 3.3.

3.3 Initial Testing of Non-Aerosol Products and the Liquid Portion of Aerosol Products

The liquid, solid, or gel product sample is analyzed to determine the total volatile material present in the sample and to determine the presence of any exempt or prohibited compounds. This analysis is conducted by performing the following tests:[1]

3.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using US EPA **Reference** Method**s** 24/24A, ASTM D 2369-**97** ~~**87**~~.

3.3.2 Determination of sample water content. For determination of water content either ASTM D 4017-**96a** ~~**88**~~, or ASTM D 3792-**91** ~~**86**~~ may be used, or results from both procedures may be averaged and that value reported.

3.3.3 Determination of ammonium content using ASTM D 1426-93 or US EPA Method 300.7.

3.3.4 Determination of ketones and alcohol content using NIOSH **Method** 1400.

3.3.5 Analysis of exempt and prohibited compounds, if present (US EPA **Reference** Method 18, US EPA Method 8240**B**, **US EPA Method 8260B**, ASTM D 859-**94** ~~**88**~~, NIOSH **Method** 1400).

3.3.6 If LVP-VOC status is claimed or the analysis indicates the presence of an LVP-VOC component and the percent VOC is not in compliance, the Executive Officer will request formulation data as specified in Section 3.5.2.

3.4 Prohibited Compounds

If the sample is found to contain compounds prohibited by ARB regulations (i.e., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

3.5 Initial Determination of VOC Content

The Executive Officer will determine the VOC content pursuant to sections 3.2 and 3.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

3.5.1 Using the appropriate formula specified in section 4.0, the Executive Officer will make an initial determination of whether the product meets the applicable VOC standards specified in ARB regulations. If initial results show that the product does not meet the applicable VOC standards, the Executive Officer may perform additional testing to

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[1] Alternate test methods may be used, as provided in section 6.0

confirm the initial results.

3.5.2 If the results obtained under section 3.5.1 show that the product does not meet the applicable VOC standards**,** the Executive Officer will request the product manufacturer or responsible party to supply product formulation data. The manufacturer or responsible party shall supply the requested information. Information submitted to the ARB Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in Title 17, California Code of Regulations, sections 91000 to 91022.

3.5.3 If the information supplied by the manufacturer or responsible party shows that the product does not meet the applicable VOC standards, then the Executive Officer will take appropriate enforcement action.

3.5.4 If the manufacturer or responsible party fails to provide formulation data as specified in section 3.5.2, the initial determination of VOC content under this section 3.5 shall determine if the product is in compliance with the applicable VOC standards. This determination may be used to establish a violation of ARB regulations.

3.6 Determination of the LVP-VOC status of compounds and mixtures. This section does not apply to antiperspirants and ~~deoderants~~ deodorants or aerosol coatings products because there is no LVP-VOC exemption for these products.

3.6.1 Formulation data. If the vapor pressure is unknown, the following ASTM methods ~~will~~ may be used to determine the LVP-VOC status of compounds and mixtures: ASTM D 86-96 (~~approved~~ April 10, 1996), ASTM D 850-93 (~~approved~~ April 15, 1993), ASTM D 1078-97 (~~approved~~ July 10, 1997), ~~and~~ ASTM D 2879-97 (~~approved~~ April 10, 1997), as modified in Appendix B to this Method 310, ASTM D 2887-97 (~~approved~~ April 10, 1997) and ASTM E 1719-97 (~~approved~~ March 10, 1997).

3.6.2 LVP-VOC status of "compounds" or "mixtures." The Executive Officer will test a sample of the LVP-VOC used in the product formulation to determine the boiling point for a compound or for a mixture. If the boiling point exceeds 216° C, the compound or mixture is an LVP-VOC. If the boiling point is less than 216° C, then the weight percent of the mixture which boils above 216° C is an LVP-VOC. The Executive Officer will use the nearest 5 percent distillation cut that is greater than 216° C as determined under 3.6.1 to determine the percentage of the mixture qualifying as an LVP-VOC.

3.6.3 Reference method for identification of LVP-VOC compounds and mixtures. If a product does not qualify as an LVP-VOC under 3.6.2, the Executive Officer will test a sample of the compound or mixture used in a products formulation utilizing one or both of the following: ASTM D 2879-97, as modified in Appendix B to ~~ARB~~ this Method 310, and ASTM E 1719-97, to determine if the compound or mixture meets the requirements of Title 17, CCR, section 94508 (78)(A).

3.**7**6 Final Determination of VOC Content

If a product's compliance status is not satisfactorily resolved under section**s** 3.5 **and 3.6**, the Executive Officer will conduct further analyses and testing as necessary to verify the formulation data.

3.**7**6.1 If the accuracy of the supplied formulation data is verified and the product sample is determined to meet the applicable VOC standards, then no enforcement action for violation of the VOC standards will be taken.

3.**7**6.2 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacture**r** or responsible party to supply information to explain the discrepancy.

3.**7**6.3 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the supplied formulation data, then the results of Method 310 shall take precedence over the supplied formulation data. The results of Method 310 shall then determine if the

product is in compliance with the applicable VOC standards, and may be used to establish a violation of ARB regulations.

4 CALCULATION OF VOC CONTENT

4.1 Aerosol Products

For aerosol products, the percent VOC content shall be calculated using the following equation:

$$\text{PERCENT VOC} = \frac{\text{WL (TV} - \text{A} - \text{H} - \text{EL)} + \text{WP} - \text{EP}}{\text{WL} + \text{WP}} \times 100\%$$

Where[2]:

WL = weight (gm) of liquid product excluding container and packaging

TV = weight fraction of non-propellant total volatile material (US EPA **Reference Methods** 24/24A, ASTM D 2369-**97** ~~**87**~~)

A = weight fraction of ammonia (as NH_4) in liquid (ASTM D 1426-93) or US EPA Method 300.7

H = weight fraction of water in liquid (ASTM D 3792-**91** ~~**86**~~ or ASTM D 4017-**96a** ~~**88**~~)

EL = weight fraction of exempt compounds in liquid (US EPA Method 8240**B**, **US EPA Method 8260B**, US EPA **Reference** Method 18, ASTM D 859-**94** ~~**88**~~, NIOSH **Method** 1400, **ASTM D 86-96, ASTM D 850-93, ASTM D 1078-97, ASTM D 2879-97, as modified in Appendix B to this Method 310, ASTM D 2887-97, ASTM E 1719-97. LVP-VOCs are exempted in accordance with section 94508(a)(78).**

WP = weight (gm) of propellant (ASTM D 3074-**94** ~~**72**~~ [as modified and include ASTM D 3064-89] or ASTM D 3063-**94** ~~**79**~~ [as modified and include ASTM D 3064-89])

EP = weight (gm) of exempt compounds in propellant (US EPA **Reference** Method 18)

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[2] Alternate test methods, as provided in 6.0, or appropriate approved methods from section 2.0 may be used.

4.2 Non-Aerosol Products

For non-aerosol products, the percent VOC content shall be calculated using the following equation:

$$\text{PERCENT VOC} = (TV - A - H - EL) \times 100\%$$

5 METHOD PRECISION AND ACCURACY

The precision of Method 310 was evaluated using seven representative products with known volatile organic compound (VOC) contents ranging from 6.2 to 81.2 percent VOC by weight. Each sample was divided into six portions, and each portion was separately analyzed to determine the VOC content. Based on the results of this analysis, the 95 percent confidence interval for Method 310 is 3.0 percent by weight (Wt/Wt%).

6 ALTERNATE TEST METHODS

Alternative test methods which are shown to accurately determine the concentration of VOCs or constituent components in antiperspirant/deodorants, consumer products, or aerosol coating products (or their emissions) may be used upon written approval of the Executive Officer.