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EPA

A GUIDELINE FOR GRAPHIC ARTS CALCULATIONS

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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ABSTRACT

The calculation of volatile organic compound emissions from graphic arts operations to determine compliance is often a complicated task, sometimes creating confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. EPA guidance for submitting data on ink formulations and performing basic calculations is contained in the document entitled "Procedures for certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings," EPA 450/3-84-019, published in December 1984. On June 19, 1985, two pages, III-4 and III-9, were revised and issued.

"A Guideline for Graphic Arts Calculations" takes the above guidance process one step further. Example calculations are included for basic emission problems, compliance determinations, control strategy problems, and complex emission problems.

SECTION 1

INTRODUCTION

1.1 PURPOSE

The purpose of this document is to provide background information, a process description, emissions data, a regulatory description, and example calculations for the graphic arts industry. This section covers the first four of these topics to provide the reader with the necessary information for calculating compliance problems. The remaining sections present sample calculations typical of those used to determine compliance or to evaluate control strategies. These calculations include explanations that are useful to persons familiar with graphic arts operations. Section 2 provides basic data considerations that are required to perform these calculations. Section 3 provides basic reformulation calculations to introduce the basic mathematical concepts involved in calculating volatile organic compound (VOC) emissions from graphic arts sources. Section 4 illustrates calculation techniques to use when a printer chooses to reduce emissions with add-on control systems. Section 5 presents reformulation and add-on control compliance calculations. These problems introduce complicating factors such as multiple printing lines and dilution solvent and are therefore more complicated than the problems in Sections 3 and 4. Section 6 includes complex calculations, which incorporate the techniques demonstrated in Sections 3, 4, and 5 plus multiple inks on multiple printing presses. Section 7 demonstrates calculations using the newly developed alternate emission limit which is available through a SIP revision.

1.2 PROCESS DESCRIPTION

The graphic arts industry includes five common types of printing: rotogravure, flexography, silk screening, letterpress, and lithography (offset). The U.S. Environmental Protection Agency (EPA) issued Control Techniques Guidelines (CTGs) to provide information to state and local air pollution control agencies on the rotogravure and flexographic industries.(1) Rotogravure and flexography are therefore commonly regulated by State Implementation Plans (SIPs) and are the subject of this document.

Rotogravure printing is considered by EPA to consist of two different categories: publication rotogravure and packaging rotogravure. Publication rotogravure is the printing of paper which is used in books, magazines, catalogs, etc.(2) These facilities are usually very large in size. Packaging rotogravure is the printing of paper, foil, and plastic film used to package various products. It is done by a considerably larger number of companies ranging from large facilities with many press units to very small captive operations with only one or two press units. Many processes normally included within the paper, fabric, or vinyl coating CTG categories may be regulated under Graphic Arts Regulations if the coating line includes a rotogravure or flexographic printing station. The State SIP should be checked to determine which requirements are applicable for a specific source.

1.2.1 Equipment

Larger printing operations use presses which have a curved image carrier mounted on a rotating cylinder, or an etched or engraved image directly on a rotating cylinder. In direct printing, the image is transferred directly from the cylinder to the print surface. In indirect printing, the image is transferred to an intermediate roll called a "blanket" and then to the print surface.(3)

Flexographic printing is the application of words, designs, and pictures to a substrate by means of a roll printing technique. The applied pattern is raised above the printing roll and the image carrier (plate) is made of rubber or another elastomeric material. A feed cylinder rotates in a trough of ink, called an ink fountain, and delivers the ink to the plate via distribution rollers. The web passes between the inked plate and the impression cylinder. As the impression cylinder presses the substrate against the inked plate, the image is printed on the substrate. The ink dries by evaporation mainly. Evaporation is achieved by moving the web through a dryer with temperatures below 120°C. (See Figure 1.) Flexographic presses are usually rotary web in design, i.e., roll-fed. However, presses that print corrugated paper board are

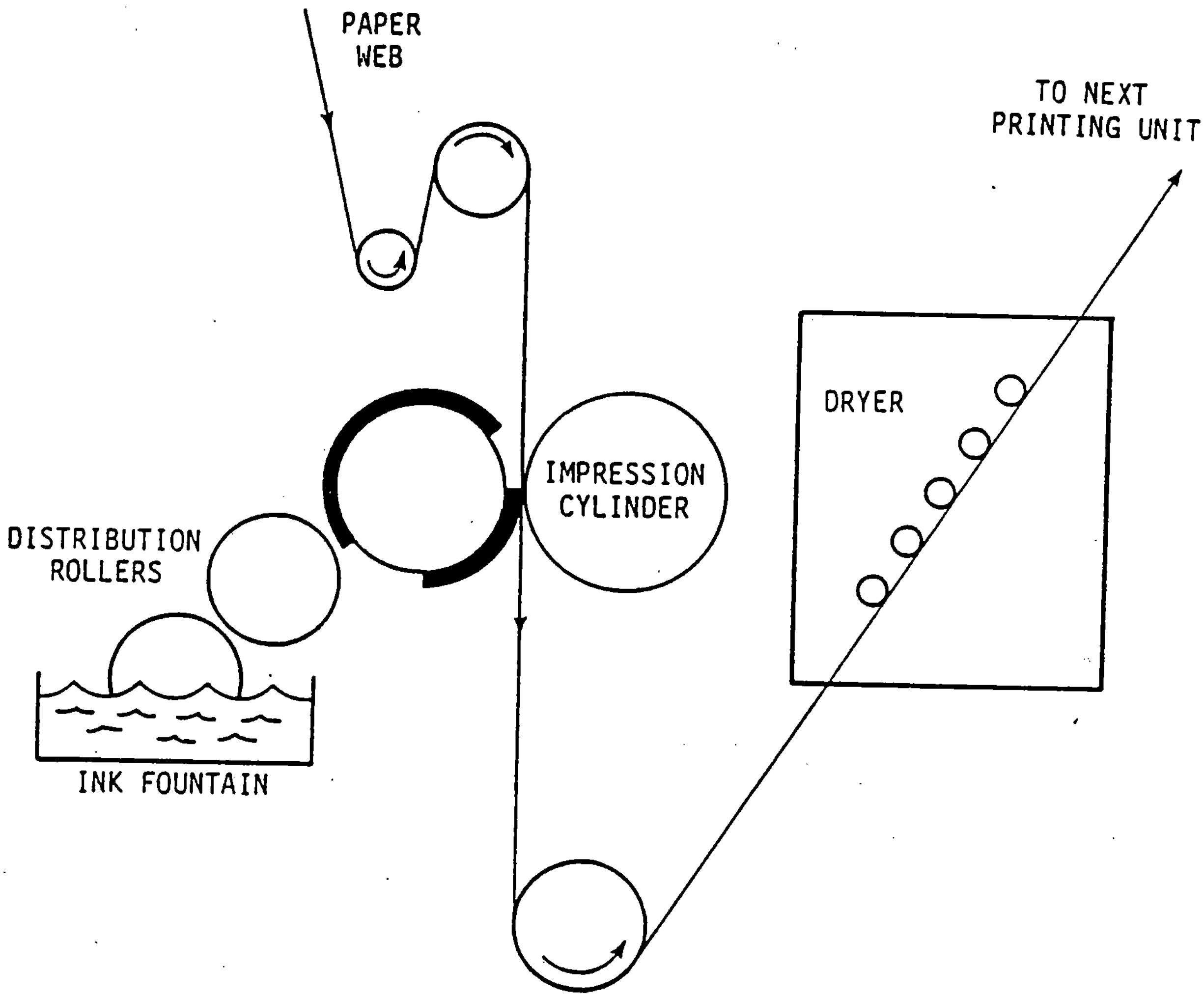

Figure 1. Flexographic printing unit.(4)

one exception. Flexography uses fluid inks (low viscosity), typically about 75 volume percent organic solvent. Obviously, any solvents used must be compatible with rubber and other plate materials.(5)

In rotogravure printing, a pattern is etched into the chrome- or copper-plated gravure cylinder. Chrome-plated cylinders provide better wear resistance. The image is in the form of cells or cups mechanically or chemically etched in the surface. These cells are usually 0.0014 inches deep by 0.005 inches square with approximately 22,500 cells per square inch. The gravure cylinder rotates in an ink trough or fountain, and the excess ink is wiped by a steel doctor blade. Then, a rubber impression cylinder (blanket) presses the web into the etched cylinder to transfer the image. Rotogravure printing also requires very fluid inks with a solvent content ranging from 50 to 85 volume percent or higher. The solvent is evaporated in low-temperature dryers, 38 to 93°C. Dryers may be of the steam drum type or may be heated indirectly by steam or hot air. (See Figure 2.)(6)

1.2.2 Ink Materials

Printing inks are composed of the same type of ingredients as surface coatings: solids, VOC, negligibly photochemically reactive (exempt) solvent, and water. Of course, they are tailored to have different properties than coatings. The solids contained in an ink consist of pigments, resins, and other materials that influence the consistency of the ink. In addition to regulatory limitations required by EPA, OSHA, FDA, and USDA, the specifications for an ink are governed by a number of considerations such as: printing processes and methods; kind of press; paper or other substrate; drying process; desired finish: matte, gloss, etc.; end use of the printed product; color; fabrication method to which the printed stock will be subjected; and sequence of ink application in multicolor printing.(7)

The VOC content of inks varies widely. Flexographic and gravure inks contain 50 to 85 volume percent VOC and dry by solvent evaporation. Water-borne inks contain a volatile mixture that is water plus 5 to 30 volume percent VOC.(8) Some water-borne inks recently developed do not contain any VOC.

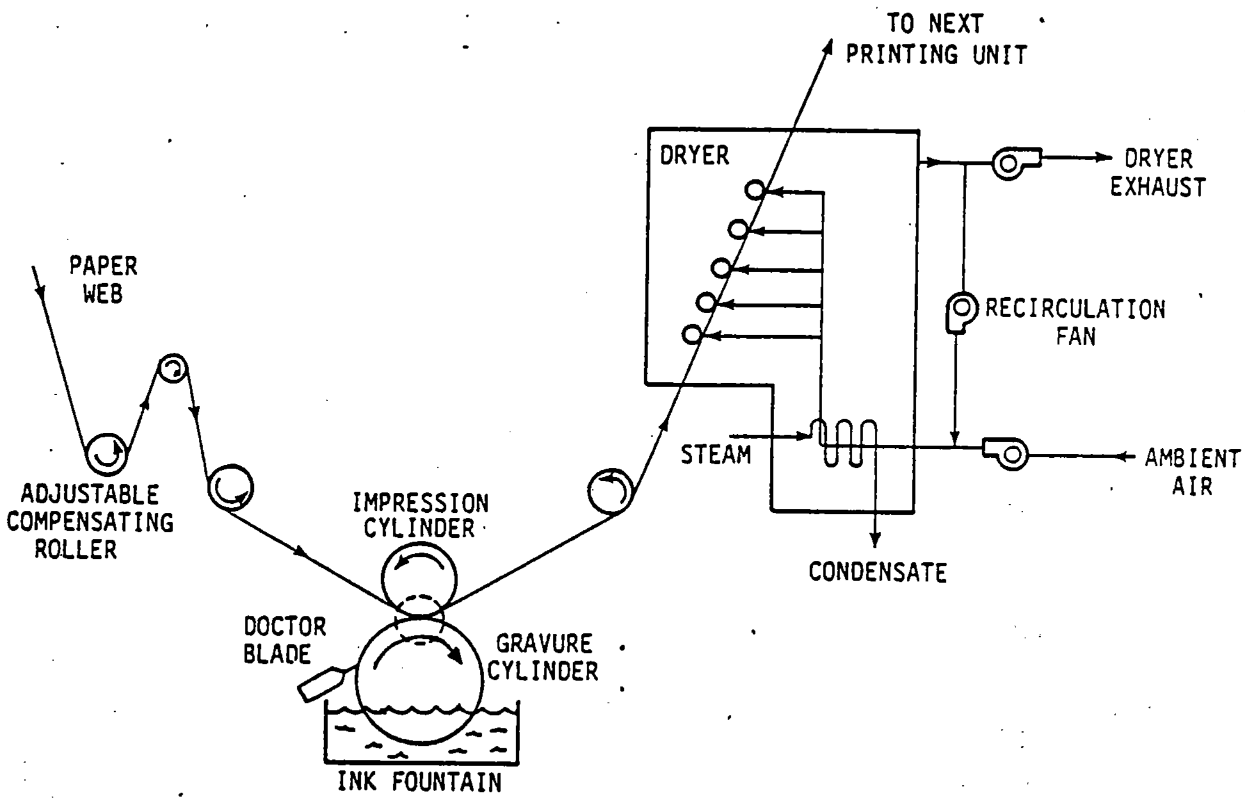

Figure 2. Rotogravure printing unit.(9)

The following solvents are representative of those used in printing inks, usually in combinations:(10)

Toluene	Ethanol
Xylene	Butanol
Heptane	Glycols
Isooctane	Glycol ether esters
Mineral Spirits	Glycol esters
Naphtha	Acetone
Hexane	Methyl ethyl ketone
Propanol	Isopropyl acetate
Isopropanol	Normal propyl acetate
Methanol	Ethyl acetate

A volatile organic compound is defined in 40 CFR Subpart A, General Provisions, §60.2, as any organic compound which participates in atmospheric photochemical reactions; or which is measured by a reference method, an equivalent method, or an alternative method; or which is determined by procedures specified under any subpart. Negligibly photochemically reactive solvents are used in inks to decrease drying time yet they do not contribute to the total VOC emissions tally. These materials should not be counted as VOCs if they are "exempt" from the applicable regulation. The method for discounting these materials is described in Appendix A. The EPA considers the following organic solvents to have negligible photochemical reactivity, and therefore does not consider them to be VOCs.

Methane*
Ethane*
1,1,1-trichloroethane (methyl chloroform)*
Methylene chloride**
Trichlorofluoromethane (CFC-11)***
Dichlorodifluoromethane (CFC-12)***
Chlorodifluoromethane (CFC-22)***
Trifluoromethane (CFC-23)***
Trichlorotrifluoroethane (CFC-113)*
Dichlorotetrafluoroethane (CFC-114)***
Chloropentafluoroethane (CFC-115)***

Many states also do not consider some or all of these materials to be VOCs.(11)

* 42 FR 35314, July 8, 1977
** 45 FR 32042, June 4, 1979
***45 FR 48941, July 22, 1980

1.3 EMISSIONS

Graphic arts operations are significant volatile organic compound (VOC) emission sources. Most inks contain VOCs which evaporate during the ink application and curing processes, rather than becoming part of the dry film. An EPA study states that the majority of VOC emissions from the flexographic printing industry are produced by large facilities, each emitting more than 1,000 tons per year of VOCs.(12) This study did not include the publication rotogravure industry, but the data listed below are considered to be representative of the regulated graphic arts industries since most publication rotogravure facilities also emit more than 1,000 tons per year.(13)

Facilities with total VOC emissions less than	Percent of total industry VOC emissions
50 tons per year	<1.0
125 tons per year	<2.7
250 tons per year	<7.6

Although the industry is quite diverse with many small facilities, the regulated industries consist of several hundred large sources.

The VOC emission points in graphic arts sources are the printing unit where ink application and dilution solvent addition occur, the ovens where solvent evaporates from the product, and the control device. Regulatory requirements discussed in the next section limit emissions by specifying the nonvolatile portion of the ink, the volatile fraction of the ink, or the overall percent reduction by the control system.

1.4 REGULATIONS

The following is a summary of the RACT regulations which control volatile organic compound (VOC) emissions from a packaging rotogravure, publication rotogravure, or flexographic printing facility that uses VOC-containing ink and emits a combined weight of VOCs greater than or equal to 100 tons per year. The applicability cutoff of 100 tons per year is based upon either historical ink and VOC use or annual potential emissions, depending on the applicable regulations. Differences exist from state to state. The regulations are enforced on an ink-by-ink basis when add-on controls are not used or process line basis if add-on controls are used unless the facility complies through a bubble as defined in a specific SIP. Generally, the regulated facility may not operate unless:

1. A carbon adsorption or incineration system is operated to reduce the volatile organic compound emissions from an effective capture system by at least 90 percent. The capture system must ensure an overall reduction in volatile organic compound emissions of at least the following percentages:

   a. 75 percent for a publication rotogravure process;
   b. 65 percent for a packaging rotogravure process;
   c. 60 percent for a flexographic printing process; or

2. The volatile fraction of the ink, as it is applied to the substrate, contains 25 percent by volume or less of VOC and 75 percent by volume or more of water; or

3. The ink as it is applied to the substrate, less water, contains 60 percent by volume or more of nonvolatile material.(14)

4. The EPA has recently developed an equivalent alternate compliance method for flexographic and packaging rotogravure printing industries only. A SIP revision is required to use this method. Please see Section 4 for more information.

Please note the following regarding Number 3 listed above. While the "less water" applies in a majority of states, some SIPs do not include it. The State SIP should be checked to determine which requirements are applicable for a specific source.

Only the compounds listed in Section 1.2.2 and any compounds given the status of "negligibly photochemically reactive" by the U.S. EPA in a future Federal Register may be considered as exempt from Federal enforcement of applicable State SIP VOC regulations. Also, Rule 66 or similar regulations based on solvent substitution and reactivity should not be referenced for exempting compounds as per 42 FR 35314, July 8, 1977.(15) For the purpose of determining compliance, negligibly photochemically reactive solvents should be treated just like water.

There are two graphic arts categories covered by New Source Performance Standards (NSPS). These are publication rotogravure and flexible vinyl and urethane coating and printing. The publication rotogravure regulation applies to printing presses modified or constructed after October 28, 1980. It limits

VOC emissions to 16 percent of the total mass of VOC solvent and water used at the facility during any one performance averaging period. The water used includes only that water contained in the water-borne raw inks and related coatings and the water added for dilution with water-borne ink systems. The flexible vinyl and urethane coating and printing NSPS regulation applies to each rotogravure printing line used to print or coat flexible vinyl or urethane products which was modified or constructed after January 18, 1983. The standard states that the owner or operator must either use inks with a weighted average VOC content less than 1.0 kilogram VOC per kilogram ink solids or reduce VOC emissions to the atmosphere by 85 percent from each affected facility.(16)

In addition to the capture and control system option, emissions from flexographic and rotogravure presses may be reduced by reformulation. Water-borne inks contain about 75 percent less VOC than conventional inks. (This number can vary from 65 to 100 percent.) These water-borne inks are used extensively in printing corrugated paperboard for containers or multi-walled bags and other packaging materials made of paper. Only a limited amount of water-borne ink can be put on thin stock before the paper will be seriously weakened. Some printing systems may be able to use water-borne inks for complete coverage but still require some solvent-borne inks for printing smaller designs which partially cover the web. In complete coverage, large areas of a given color are applied; however, in partial coverage a thin strip of a given color is applied and more precision is required. High solids inks have met with little success in rotogravure and flexographic printing due to the design of the process. However, research is being conducted in the development of a high solids ink which is compatible with existing equipment.(17)

1.5 CALCULATIONS

The remaining sections in this document present sample calculations typical of those used to determine compliance or to evaluate control strategies. These step-by-step calculations are accompanied by explanations that are useful to persons familiar with graphic arts operations. Basic calculations are included along with a variety of more complex problems to demonstrate emission calculations for different scenarios.

The basis for most of the sample calculations is the information and procedures discussed in Procedure for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings, EPA-450/3-84-019, December 1984, which is reprinted as Appendix A of this report and referred to as the "VOC Data Sheets". On June 19, 1985, two pages, III-4 and III-9, were revised and issued. The first VOC Data Sheet provides information on the VOCs present in a coating or ink when it is sold by the manufacturer to the coater or printer. This is referred to as the VOC content of the coating "as supplied by the coating manufacturer to the user." The second VOC Data Sheet provides information on the VOCs present in the coating or ink as it is used by the coater or printer and includes the effect of dilution solvent added before application. This is referred to as the VOC content of the coating "as applied to the substrate by the user." The calculations in this document assume that the inspector has obtained the ink data from the VOC Data Sheets or an EPA Reference Method 24 or 24A test as appropriate. It is up to the inspector to verify data. EPA Reference Method 24A is applicable to publication rotogravure inks only. Reference Method 24 data is acceptable for all other inks. However, the appropriate SIP should be checked to verify which test method is required. Appendix B contains a copy of Reference Methods 24 and 24A.

To comply with the VOC regulations, a printer might elect to reformulate to a low VOC content ink or to use add-on controls such as incineration or carbon adsorption. VOC compliance or non-compliance can be established through calculations based on either the efficiency of the control system or the composition of the ink. For example, in cases where compliance is achieved by use of water-borne or high solids ink, compliance can be determined through calculations based on analysis of the ink and formulation data. When add-on controls are used, more complex stack and capture tests and calculations can be performed to determine the effectiveness of the control system.

In both flexographic and rotogravure printing, VOC may be introduced to the system in the ink (either in the ink as supplied, as a diluent, or to make-up for evaporative losses) and as a cleaning agent.(18) VOC introduced as a cleaning agent is not normally included in the total VOC emissions tally. However, sometimes cleaning solvent is included when the facility complies with the regulations through alternate means (e.g., a bubble). To reduce emissions, a capture system and a control device may be used. The two add-on control systems used primarily on flexographic and rotogravure printing are carbon adsorption and incineration.(19) Condensation, a third add-on control, is also used but this method is not as effective in reducing emissions. With carbon adsorption, VOCs which are water miscible must be separated from the water, usually by distillation. Plants that use incineration as a control method attempt to minimize the expense by recovering as much of the heat as practical for use elsewhere in the plant such as drying ovens.

Two compounds, 1,1,1-trichloroethane and methylene chloride, are used as solvents in some inks but are considered negligibly reactive by EPA and are exempt from regulation in most SIPs. The method for discounting these materials is described in some of the examples and in Appendix A. Generally, these materials, when "exempt" from the applicable regulation, are treated in the same manner as water in emission calculations.(20)

The overall efficiency of the control system is a product of the capture system efficiency and the control device efficiency. It is more difficult to capture VOC emissions from a flexographic press than a rotogravure press due to the construction design of flexographic presses. Flexographic printing units and dryers are mounted compactly such that effective hooding and ducting are difficult to construct without resorting to a total enclosure. Rotogravure printing units and dryers are mounted such that hoods and ducts can be constructed. VOCs which are captured may be routed to the control device. VOCs which are not captured can be emitted as fugitive emissions, retained in the product, or disposed. If waste VOCs are improperly disposed of, they can be emitted as fugitive emissions. VOC initially retained in the product usually is released over time and therefore, is considered an emission in compliance calculations.

The following sections contain sample calculations. Section 3 contains three basic calculations. The purpose of these problems is to familiarize the reader with the regulatory requirements by determining the compliance status of the inks. Section 4 includes three control strategy calculations. One compliance option is to use add-on control systems. These problems present various VOC control strategies and demonstrate how to calculate emissions to determine compliance. Section 5 presents three compliance determination calculations. Examples 2 and 3 are more difficult than the basic and control strategy calculations because they incorporate multiple printing lines and a variety of compliance techniques. Section 6 contains two complex calculations. These problems incorporate multiple lines, inks, add-on controls, complying inks, and noncomplying inks. All factors must be considered and a series of calculations must be completed. The sections progress from simple to complex so the reader can master the basics and then progress to more difficult scenarios.

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3. Ibid pp. 2-1, 2-2.

4. Enforceability Aspects of RACT for the Rotogravure and Flexography Portion of the Graphic Arts Industry. PEDCo Environmental, Inc. prepared for the U.S. Environmental Protection Agency, Division of Stationary Source Enforcement. Under Contract No. 68-02-4147, Task No. 123. March 20, 1980, p. 6.

5. Control of Volatile Organic Emissions from Existing Stationary Sources - Volume VIII: Graphic Arts - Rotogravure and Flexography. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. EPA-450/2-78-033. OAQPS No. 1.2-109. December 1978. p. 2-2.

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14. Ibid.

15. A Guideline for Surface Coating Calculations. Prepared by PEI Associates, Inc. for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. May 1986. p. 4.

16. New Source Performance Standards. 40 CFR Part 60. Subpart QQ, Standards of Performance for the Graphic Arts Industry: Publication Rotogravure Printing and Subpart FFF, Standards of Performance for Flexible Vinyl and Urethane Coating and Printing.

17. Control of Volatile Organic Emissions from Existing Stationary Sources - Volume VIII. Graphic Arts - Rotogravure and Flexography. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. EPA-450/2-78-033. OAQPS No. 1.2-109. December 1978. pp. 3-9, 3-10.

18. Guidance to State and Local Agencies in Preparing Regulations to Control Volatile Organic Compounds from Ten Stationary Sources. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. EPA-450/2-79-004. September 1979. p. 92.

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20. Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. EPA 450/3-84-019. December 1984. pp. II-3, III-5.

SECTION 2

BASIC DATA CONSIDERATIONS

Before doing any calculations, it is appropriate to consider the data needed to perform these calculations and their availability. The graphic arts standard in the applicable SIP should be considered first to confirm the applicability and specific requirements of the standard. Compliance requirements vary depending on the control strategy being implemented.

If add-on controls are used, compliance must usually be based on a stack test and a capture efficiency test on each affected line. The control device efficiency determined by the stack test multiplied by the capture efficiency equals the overall efficiency of the control system. In most cases, this result can be compared directly to the standard which is expressed as an overall efficiency. Once a source demonstrates compliance in this manner, compliance is checked by monitoring the operating conditions of the control system to ensure they are consistent with those recorded during the compliance test. If there is a significant change in these conditions or the plant's method of operation, or if the integrity of the control system is in question, the source should be retested to confirm compliance under the new operating conditions. Where the control device is a carbon adsorption system, compliance may be demonstrated by conducting a liquid material balance (total VOC used versus total VOC recovered). Compliance can usually be checked by reviewing plant records over some convenient period of time, preferably coinciding with a line (or plant if appropriate) shutdown (e.g., on a weekend) or process turnaround. This avoids problems associated with determining the amount of material (VOC) in process, since the amount of ink in fountains and reservoirs on a press is difficult to measure. The carbon adsorber should also be regenerated to assure that all adsorbed VOC has been desorbed and transferred to the recovery tank and is not in the carbon bed where it can not be measured.

If add-on controls are not used, the inks used must comply with either the water-borne or high solids standard. Since the high solids standard is usually expressed as the volume percent solids in the ink less water, a water-borne ink which does not comply with the water-borne standard must also be evaluated with regard to the high solids standard.

Most SIP's high solids and water-borne ink standards are based on the condition of the ink as it is applied to the substrate. The best way to determine compliance with such standards is to use the results of a Reference Method 24 (RM-24) or 24A analysis of the ink taken from the press fountain or reservoir and additional ink and dilution solvent formulation information. Most of the information needed to determine compliance can be found on the "as applied" VOC data sheet. These data include the volume percent solids, volume percent water, density of the ink and weight fraction VOC. The volume percent solids of the as applied ink can be calculated (see equations III-6, III-7, III-8, and III-12 in Appendix A), but the density and volume percent solids of the as supplied ink and the density of the dilution solvent must be known to do these calculations. This information is available on either the "as supplied" or "as applied" VOC data sheets. If the data sheets are not used, the inspector may have to perform these calculations. In cases where additional VOC is added during a press run to make up for evaporative losses which occur at the press fountain or reservoir, then a different result may be obtained if the calculations are done using RM-24 (or 24A) analysis of the as supplied ink and records of all dilution and make-up solvent added during a press run. The method which should be used will depend on the specific SIP requirement. If the standard is based on the ink as applied, the as applied analysis is appropriate. If the standard requires that accumulated additions be considered, as supplied data and dilution records must be used.

If the applicable SIP standard requires that all solvent additions (dilution and make-up solvent) be considered, the "as supplied" data sheet and plant records must be used. The procedure for calculating the volume of solids applied for an ink "as applied" standard does not apply since that calculation does not fully account for make-up solvent. If plant records are not adequate to document all solvent additions, steps must be taken to correct this problem before a compliance determination can be made.

The volume percent of VOC is also needed but is not stated on the VOC data sheets, nor is it determined by RM-24 (or 24A) analysis. The weight percent

VOC is stated. To convert the weight percent to volume percent, the density of the VOC must be determined. If a sample of just the solvent or solvent blend in the ink as applied can be obtained, then a density can be determined analytically via ASTM D1475. If this is not possible or practical, an average density can be estimated from formulation data using equations III-2 and III-3 in Appendix A. Note that these equations, as stated in the appendix, are used to calculate the density of only the dilution solvent. To perform the calculation suggested here, the values for each VOC used for dilution (to make-up for evaporation losses) and in the as supplied ink formulation must be included. If available data is not sufficient to perform this calculation, it is suggested that the density of the dilution solvent (VOC portion only) be used as a representative density. This value is stated on the "as applied" VOC data sheet.

In most instances, only RM-24 (or 24A) analysis results for an ink sample taken from the press "as applied" are available. To estimate the ink parameters needed to determine compliance, the volume of solids is often calculated by assuming that volumes are additive. This method is often called "back calculating" volume of solids. It introduces a potential error into the calculation since volumes are not truly additive. As a result, the volume of solids may be understated. This method should only be used if all other methods are not implementable. To perform the calculation, some VOC formulation data must be provided by the source to determine the density of the VOC. As noted before, this density is needed to convert the weight percent VOC result from RM-24 (or 24A) to a volume percent. Once the volume percent of each component other than solids is known (i.e., VOC, water and exempt solvent), the volume of solids is calculated by subtracting the sum of all other components (volume percent) from 100 percent. The result is the volume percent solids based on the assumption that volumes are additive.

Caution must be exercised when results calculated in this manner are used to determine compliance. To compensate somewhat for the error introduced by the assumption, it is suggested that the highest density indicated for any VOC present in the ink be used to calculate the volume of solids. This would result in a minimum calculated value for VOC and a maximum calculated value for volume of solids. Therefore, the results would tend to give the best possible situation for the source to demonstrate compliance.

The validity and accuracy of compliance calculations are always enhanced if good operating data and material-use records are available. This is especially true for graphic arts sources. The regulatory agency should take steps to assure that records are generated and maintained by a source and that these records are adequate to determine compliance with the SIP standard. Where non-compliance is evident by the back calculation method, but existing records are less than adequate for a more comprehensive evaluation, the source, at a minimum, should be required to maintain the necessary records for a specific period of time to confirm its compliance status.

One last point must be considered before proceeding with the calculations. The terms "VOC" and "solvent" have been used rather indiscriminately in the past. An effort has been made to correct for this but problems are still evident. The term VOC as defined by EPA (see page 6) would include most organic solvents, but is not limited to just organic solvents. In practice, RM-24 (or 24A) test results may actually define VOC; that is organic compounds which volatilize under test conditions are VOCs. Virtually all organic solvents would volatilize under test conditions. However, other organic compounds, which are not solvents by definition, and products of chemical reactions taking place at test conditions may also contribute to the amount of VOC determined by the test.

The terms "dilution solvent" and "make-up solvent" are used in this text to be consistent with terms used by the industry. For the most part, the VOCs used for these purposes are being used as solvents. However, when considering formulation data, be aware that the sum of all the components called "solvents" may not actually be the total amount of VOC present or that would be determined by an appropriate test.

SECTION 3

BASIC REFORMULATION CALCULATIONS

The purpose of this section is to familiarize the reader with the regulations by presenting three basic examples. The examples show how to determine the volume of VOC and water in the volatile portion of the ink and volume of solids in the ink to check for complying ink formulations. Example 1 presents ink data for a packaging rotogravure printer. The problem states the applicable regulation and asks if the plant is in compliance. Example 2 presents ink data for a flexographic printer. The printer's ink, less water, must contain 60 percent by volume or more of nonvolatile material. The problem asks if the printer is in compliance with the regulation. Example 3 presents ink data for a publication rotogravure printer. The problem asks how the printer can comply with the regulations.

Example 1 -

A packaging rotogravure printing plant uses one ink whose composition as applied in volume percent from Method 24 testing, manufacturer's data and calculations from the VOC Data Sheets (See Appendix A) is 10 percent non-volatiles, 20 percent VOC and 70 percent water. The press that uses this ink is uncontrolled. Is it in compliance?

The regulation states that a packaging rotogravure printing operation must reduce VOC emissions by 65 percent or use an ink which contains, less water, 60 percent by volume or more of nonvolatile material or use an ink whose volatile fraction contains 25 percent by volume or less of VOC solvent and 75 percent by volume or more of water.

The volume percent of nonvolatile material less water is

$$\frac{10\%\ \text{nonvolatiles}}{100\%\ \text{ink} - 70\%\ \text{water}} \times 100 = 33\%$$

Since the nonvolatile material does not exceed 60 percent by volume, less water, and the press is uncontrolled, check to see if the plant complies with the third part of the regulation.

The volume percent of VOC in the volatile fraction of the ink is

$$\frac{20\%\ \text{VOC}}{20\%\ \text{VOC} + 70\%\ \text{water}} \times 100 = 22.2\%.$$

The volume percent of water in the volatile fraction of the ink can be calculated by either of the following two ways:

$$\frac{70\%\ \text{water}}{20\%\ \text{VOC} + 70\%\ \text{water}} \times 100 = 77.8\%$$

or

$$100\% - 22.2\% = 77.8\%.$$

Therefore, the press is in compliance with the third part of the regulation.

Note: Data provided from the reference test methods include the following "as applied" data: the ink density $(D_i)_a$, weight fraction of total volatiles $(W_v)_a$, and weight fraction of water $(W_w)_a$. Manufacturer's formulation data includes volume percent of each non-volatile component $[(V_n)_{s_i}]$, and name and either the mass or volume of each VOC present. The source provides the density of the dilution solvent. From this data, the following may be calculated (as per Appendix A):

Volume percent water

$$(V_w)_a = \frac{(W_w)_a \quad (D_i)_a}{D_w}$$

where D_w = 8.33 lbs/gal

Weight percent volatile organics

$$(W_o)_a = (W_v)_a - (W_w)_a$$

Note: if $W_w = 0$, then $W_o = W_v$

Volume percent nonvolatiles (solids) "as supplied"

$$(V_n)_s = \sum_{i=1}^{p} (V_n)_{s_i}$$

where $(V_n)_{s_i}$ is supplied by the manufacturer

and p is equal to the number of nonvolatile components in the ink.

Volume percent nonvolatiles (solids) "as applied"

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d}$$

Where Rd = the volume of VOC added per unit of ink "as supplied". In the absence of adequate dilution records, Rd can be calculated from entries on the VOC data sheets, see Page III-7, Appendix A for additional information.

Density of VOC "as applied"

$$(D_o)_a = \frac{100\%}{\sum_{j=1}^{m} \frac{W_j}{D_j}}$$

or

$$(D_o)_a = \frac{1}{100\%} \sum_{j=1}^{m} V_j \, D_j$$

Where D_j, W_j, and V_j denote the density, weight percent and volume percent of each VOC (including dilution VOC) in the ink as applied and 'm' is the number of VOCs present.

Volume percent VOC "as applied"

$$(V_o)_a = \frac{(W_o)_a \, (D_j)_a}{(D_o)_a}$$

Example 2 -

A flexographic printer uses an ink that has the following composition in weight percent: nonvolatile material 79.3% and VOC 20.7%. The compositions were obtained during Method 24 testing. The ink density is 11.0 pounds per gallon, and the VOC density is 6.0 pounds per gallon (from formulation data). Is the ink in compliance with a regulation that stipulates use of an ink which contains 60 percent by volume or more of nonvolatile material?

Since the information needed to calculate volume of solids using equation III-12 on page III-8 of Appendix A is not available, volume of solids is back calculated in this example from VOC content and VOC density. This calculation assumes that the VOC and solids volumes are additive (see Page 17).

The volume of VOC in one gallon of ink is

$$\frac{11.0 \text{ lb ink}}{1 \text{ gal ink}} \times \frac{0.207 \text{ lb VOC}}{1 \text{ lb ink}} \times \frac{1 \text{ gal VOC}}{6.0 \text{ lb VOC}} = \frac{0.38 \text{ gal VOC}}{1 \text{ gal ink}}$$

The volume percent of nonvolatile material in one gallon of ink is

$$(1 - 0.38) \times 100 = 62\%.$$

Therefore, the ink is in compliance.

Example 3 -

A publication rotogravure printer uses an ink that is 80 percent VOC and 20 percent pigments and other nonvolatiles (compositions are in weight percent). The ink has a density of 7.2 pounds per gallon. The VOC density is 6.5 pounds per gallon. All data were obtained through Method 24A analyses of the ink as applied except that the VOC density was computed from formulation data. How can this plant comply with the regulation for publication rotogravure facilities?

First, check to see if the ink meets the high solids criterium for complying inks assuming that volumes are additive.

The volume of VOC in one gallon of ink is:

$$\frac{7.2 \text{ lb ink}}{1 \text{ gal ink}} \times \frac{0.8 \text{ lb VOC}}{1 \text{ lb ink}} \times \frac{1 \text{ gal VOC}}{6.5 \text{ lb VOC}} = \frac{0.886 \text{ gal VOC}}{1 \text{ gal ink}}$$

The volume of solids in one gallon of ink is

$$1 - \frac{0.886 \text{ gal VOC}}{1 \text{ gal ink}} = \frac{0.114 \text{ gal solids}}{1 \text{ gal ink}}$$

Since the volume of solids of the ink as applied is significantly less than 60 percent by volume, the plant must install a capture and control system to reduce overall VOC emissions by at least 75 percent. If the volume of solids applied calculation had resulted in a value which approached the 60 percent level, it would have been advisable to seek additional information about the ink and perform a more exact calculation using equation III-12 on page III-8 of Appendix A.

SECTION 4

CONTROL COMPLIANCE CALCULATIONS

The two problems in this section demonstrate VOC control strategies and how to calculate emissions to determine compliance. Example 1 presents a flexographic printer which uses a solvent-based ink. Ink data and the yearly ink use rate are given. The plant uses add-on controls to control VOC emissions. The problem asks what the plant's uncontrolled VOC emissions were last year and if the plant met RACT, what were its controlled VOC emissions. Example 2 presents a publication rotogravure plant which uses different inks on its two printing lines. Data and ink use rate for each ink are provided. Two add-on control systems are being evaluated. Efficiencies for the control devices are given. The problem asks the reader to calculate what the efficiencies of the capture systems must be to achieve a VOC emission reduction of 75 percent. The problem also asks what the annual uncontrolled emissions and annual allowable emissions with the add-on control systems are from each press if the overall reduction is exactly 75 percent. Unless otherwise indicated, all solvents are considered to be VOCs.

Example 1 -

A plant uses a flexographic printing ink that is 80 percent by weight isopropanol and 20 percent by weight pigments and other nonvolatiles as applied. The ink density is 7.44 pounds per gallon. Last year, the plant used 10,000 55-gallon drums of ink. A performance test on the plant's emission control system showed a 75 percent efficiency for the capture system for each line and a 90 percent efficiency for the control device. What were the plant's potential (before control) VOC emissions last year? If the requirement is to control at least 60 percent of the VOC emissions on a line by line basis, is the plant in compliance? What would the VOC emissions have been last year if the plant just met the RACT standard? What were the actual VOC emissions last year?

The VOC content of each drum is

$$\frac{55 \text{ gal ink}}{\text{drum}} \times \frac{7.44 \text{ lb ink}}{\text{gal ink}} \times \frac{0.8 \text{ lb VOC}}{\text{lb ink}} = \frac{327.4 \text{ lb VOC}}{\text{drum}}$$

Annual potential emissions last year were

$$\frac{327.4 \text{ lb VOC}}{\text{drum}} \times \frac{10{,}000 \text{ drums}}{\text{y}} = 3{,}274{,}000 \text{ lb VOC} = 1637 \text{ Tons VOC}$$

The overall efficiency for each line = (0.75 x 0.90) x 100 = 67.5% which is greater than 60%. Therefore, each line is in compliance.

With the existing control system, the annual VOC emissions last year were

(3,274,000) x [1 - (0.75 x 0.90)] = 1,064,050 lb VOC = 532 Tons VOC.

If the emission control system had just satisfied the RACT requirement (60 percent overall efficiency), the annual VOC emissions last year would have been

(3,274,000 lb VOC) x [1 - 0.60] = 1,309,600 lb VOC = 655 Tons VOC

- -

Example 2 -

A publication rotogravure plant uses different inks on its two printing presses. Press No. 1's ink is 85 volume percent VOC and 15 volume percent pigments and other nonvolatiles as applied. Press No. 1's VOC density is 6.8 pounds per gallon. Press No. 2's ink is 80 volume percent VOC and 20 volume percent pigments and other nonvolatiles as applied. Press No. 2's VOC density is 7.2 pounds per gallon. For the coming year, the anticipated ink usage is 400,000 gallons for Press No. 1 and 600,000 gallons for Press No. 2.

The company president is evaluating two add-on control systems for the presses. For Press No. 1, the control device is guaranteed to be 95 percent efficient. For Press No. 2, the control device is guaranteed to be 98 percent efficient. If the plant must achieve a VOC emission reduction of 75 percent for each press, what efficiencies must the capture systems achieve? What are the annual potential (before control) emissions and the annual actual emissions with the add-on control systems from each press if the overall reduction is exactly 75 percent and the anticipated usage is realized.

The emission reduction achieved is the product of the efficiencies of the capture system and control device. Since the emission reduction must be 75 percent for each press, the capture system efficiencies can be calculated by dividing 75 percent by the control device efficiencies.

For Press No. 1, the capture system efficiency must be at least:

$$\frac{75\%}{95\%} \times 100 = 78.95\%$$

For Press No. 2, the capture system efficiency must be at least

$$\frac{75\%}{98\%} \times 100 = 76.53\%$$

The potential annual VOC emissions from each press are

Press No. 1

$$\frac{0.85 \text{ gal VOC}}{1 \text{ gal ink}} \times \frac{6.8 \text{ lb VOC}}{1 \text{ gal VOC}} \times \frac{400{,}000 \text{ gal ink}}{\text{yr}} = \frac{2{,}312{,}000 \text{ lb VOC}}{}$$

$$= \frac{1{,}156 \text{ Tons VOC}}{\text{yr}}$$

Press No. 2

$$\frac{0.80 \text{ gal VOC}}{1 \text{ gal ink}} \times \frac{7.2 \text{ lb VOC}}{1 \text{ gal VOC}} \times \frac{600{,}000 \text{ gal ink}}{\text{yr}} = \frac{3{,}456{,}000 \text{ lb VOC}}{\text{yr}}$$

$$= \frac{1{,}728 \text{ Tons VOC}}{\text{yr}}$$

The actual annual VOC emissions from each press would be

Press No. 1

$$\frac{2{,}312{,}000 \text{ lb VOC}}{\text{yr}} \times (1 - 0.75) = \frac{578{,}000 \text{ lb VOC}}{\text{yr}} = \frac{289 \text{ Tons VOC}}{\text{yr}}$$

Press No. 2

$$\frac{3{,}456{,}000 \text{ lb VOC}}{\text{yr}} \times (1 - 0.75) = \frac{864{,}000 \text{ lb VOC}}{\text{yr}} = \frac{432 \text{ Tons VOC}}{\text{yr}}$$

SECTION 5

FORMULATION AND CONTROL COMPLIANCE CALCULATIONS

This section provides four examples which demonstrate how to determine whether a printer is in compliance with the regulations. Example 1 presents ink data for a packaging rotogravure printer. Ink data are given which describe a higher solids ink that the printer is using. The problem asks if the printer is in compliance with a regulation that requires the ink as it is applied to the substrate, less water, to contain 60 percent by volume or more of nonvolatile material. Example 2 provides ink data and the daily ink use rate for a graphic arts facility. The problem states that two VOC control strategies are being evaluated. The reader is asked to calculate the daily emissions for each control option. Example 3 presents data for a flexographic printing plant. The facility bubbles emissions from its nine printing lines based on a SIP revision. The regulations require a 60 percent emission reduction. The plant uses add-on controls on selected printing lines to control VOC emissions. The object is to see if the actual emissions are less than or equal to the allowable emissions. The uncontrolled and actual emissions are calculated for the plant on a per-line basis and the compliance status is determined. Example 4 presents data for a packaging rotogravure plant. Dilution solvent is used at this plant. The facility bubbles its emissions based on a SIP revision. The plant uses refrigeration condensers to recover VOCs. The plant must meet RACT requirements which require overall VOC control of 65 percent. The object is to determine the solvent recovery necessary by the control system. Note that Method 24 is the regulatory test for determining the VOC content of inks. Formulation data may not be sufficient to determine compliance because of VOC additions and fugitive losses at the press. Therefore, the percent fractions of VOC and water in the press-ready ink could change. Unless otherwise indicated, all solvents are considered to be VOCs.

Example 1 -

An inspector visits a packaging rotogravure printer to obtain information for a file update. The printer has recently switched to a high solids ink. The printer gives the inspector an ink analysis sheet with the following information that is based on Reference Method 24 and data supplied by the manufacturer:

BLACK INK LOT 270A	
Pigments and other nonvolatiles supplied = $(V_n)_s$	60% by volume
VOC	30% by weight
Water	10% by weight
Ink density - supplied = $(D_i)_s$	9.3 lb/gallon
Ink density - applied = $(D_i)_a$	8.52 lb/gallon
Dilution solvent density (from formulation data) = D_d (90% VOC, 10% H_2O by volume)	6.7 lb/gallon

Is the printer in compliance with a regulation that requires the ink as it is applied to the substrate, less water, to contain 60 percent by volume or more of nonvolatile material?

To calculate the volume of solids as applied, we must calculate the volume of photochemically reactive organic solvent (VOC) added per unit volume of "as supplied" ink (R_d). Since the dilution solvent contains water, this is a two step process. First we must calculate the volume of premixed water and VOC added per unit volume of coating "as supplied" (R_d^+).

$$R_d^+ = \frac{(D_i)_s - (D_i)_a}{(D_i)_a - D_d} = \frac{9.3 - 8.52}{8.52 - 6.7} = 0.43$$

Then we can calculate R_d as follows (Note: $(V_w)_d$ = Volume percent water in dilution solvent)

$$R_d = R_d^+ \left[1 - \frac{(V_w)_d}{100\%}\right] = 0.43 \left[1 - \frac{10\%}{100\%}\right] = 0.39$$

Now we can calculate the volume of solids as applied, $(V_n)_a$ as follows

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d} = \frac{60\%}{1 + 0.39} = 43.2\%$$

Example 2 -

A flexographic printing facility uses a printing ink that is 80 weight percent VOC and 20 weight percent solids. The ink density is 7.6 pounds per gallon. The daily ink use is 900 gallons. The plant operates two eight-hour shifts with 25 percent press outage due to set-up and clean-up time.

The company president is evaluating two VOC control strategies. Option No. 1 involves adding a carbon adsorber to recover solvent. The plant must reduce VOC emissions by at least 60 percent. Option No. 2 involves switching to a waterbase ink; the ink supplier indicates that the composition by volume as applied will be 20 percent VOC, 20 percent solids, and 60 percent water. The density of the VOC in this ink is 6.6 pounds per gallon. This waterbase ink will meet the standard. The ink use rate and press outage are the same as for the high VOC content ink.

What are the daily emissions for each option?

For Option No. 1, the emission reduction must be at least 60 percent.

Daily uncontrolled emissions for this option are

$$\frac{900\ \text{gal ink}}{\text{day}} \times \frac{7.6\ \text{lb ink}}{1\ \text{gal ink}} \times \frac{0.8\ \text{lb VOC}}{1\ \text{lb ink}} = \frac{5{,}472\ \text{lb VOC}}{\text{day}}$$

The daily emissions with controls are

$$\frac{5{,}472\ \text{lb VOC}}{\text{day}} \times (1.0 - 0.6) = \frac{2{,}189\ \text{lb VOC}}{\text{day}}$$

For Option No. 2, the daily emissions are

$$\frac{900\ \text{gal ink}}{\text{day}} \times \frac{0.2\ \text{gal VOC}}{1\ \text{gal ink}} \times \frac{6.6\ \text{lb VOC}}{1\ \text{gal VOC}} = \frac{1{,}188\ \text{lb VOC}}{\text{day}}$$

Example 3 -

A job-shop flexographic printing plant has nine printing lines. The regulations allow the facility to bubble the nine printing lines through an EPA approved SIP revision. To comply with the regulations, a 60 percent emission reduction is required. Emissions from Line Nos. 3, 4, 5, and 6 are controlled by an incinerator whose VOC destruction efficiency at the time of its last performance test was 95 percent. A material balance around the ventilation system for these four lines during the performance test showed that 75 percent of the solvent emissions were captured by the ventilation system for each of these lines. The inspector verifies that the incinerator operating temperature and face velocities of the capture hoods are the same as during the performance test so he assumes that the capture and control efficiencies are unchanged. Emissions from Line Nos. 7 and 8 are ducted to a common carbon adsorber whose overall control efficiency measured at the last performance test was 62 percent for each line.

Thinning solvent is used on all lines at a rate of 10 volume percent of the ink use rate per day. The thinning solvent density is 6.6 lb per gallon. The plant's ink formulations, ink application rates, and thinning solvent use rates for one 24-hour period are shown in the following table.

Printing line	VOC density, lb/gal	As supplied ink formulations		Undiluted ink application rate, gal/day	Thinning solvent use rate, gal/day
		Volume percent solids	Volume percent VOC		
1	6.2	20.0	80.0	75	7.5
2	6.2	20.0	80.0	37.5	3.75
3	6.2	20.0	80.0	90.0	9.0
4	6.2	20.0	80.0	75.0	7.5
5	6.2	20.0	80.0	45.0	4.5
6	6.2	20.0	80.0	125.0	12.5
7	6.3	9.0	91.0	70.0	7.0
8	6.3	9.0	91.0	35.0	3.5
9	5.8	10.0	90.0	80	8.0

The uncontrolled pounds of VOC emitted per day are equal to the ink application rate (gal ink per day) times the volume fraction of VOC in the ink (gal VOC per gal ink) times the ink VOC density (lb VOC per gal VOC) plus the thinning solvent rate (gal thinning solvent per day) times the thinning solvent density (lb solvent per gal solvent).

For Line No. 1, the uncontrolled VOC emissions are

$$\left[\frac{75 \text{ gal ink}}{\text{day}} \times \frac{0.8 \text{ gal VOC}}{1 \text{ gal ink}} \times \frac{6.2 \text{ lb VOC}}{1 \text{ gal VOC}}\right] +$$

$$\left[\frac{7.5 \text{ gal thinning solvent}}{\text{day}} \times \frac{6.6 \text{ lb thinning solvent}}{1 \text{ gal thinning solvent}}\right] =$$

$$\frac{372 \text{ lb VOC}}{\text{day}} + \frac{49.5 \text{ lb VOC}}{\text{day}} = \frac{421.5 \text{ lb VOC}}{\text{day}}$$

For lines with controls, the actual pounds of VOC emitted per day are equal to the uncontrolled VOC emissions (lb per day) times one minus the control system efficiency.

For Line No. 3, the actual pounds of VOC emitted per day are

$$\frac{505.8\ \text{lb VOC}}{\text{day}} \times [1 - (0.95 \times 0.75)] = \frac{145.4\ \text{lb VOC}}{\text{day}}$$

For Line Nos. 1, 2, and 9 the actual VOC emissions equal the uncontrolled VOC emissions because these lines are not controlled.

The uncontrolled and actual VOC emissions for all nine printing lines are presented in the following table.

Printing line	Uncontrolled VOC emissions, lb/day	Actual VOC emissions, lb/day
1	421.5	421.5
2	210.8	210.8
3	505.8	145.4
4	421.5	121.2
5	252.9	72.7
6	702.5	202.0
7	447.5	170.1
8	223.8	85.0
9	470.4	470.4
TOTAL	3,656.7	1,899.1

A 60 percent emission reduction is required. Therefore, allowable VOC emissions are 40 percent of the uncontrolled VOC emissions.

0.4 x 3656.7 lb VOC/day = 1462.7 lb VOC/day.

Since the plant emitted 1899.1 lb VOC on this day, it is not in compliance.

- -

Example 4 -

A packaging rotogravure plant uses an ink concentrate (density is 10.8 pounds per gallon) that contains 30.55 percent by weight methanol (density is 6.6 pounds per gallon) and 69.45 percent by weight pigments. The ink concentrate is used on six printing lines and is diluted prior to use with isopropanol or water (isopropanol density is 6.6 pounds per gallon). A source specific SIP revision allows this facility to bubble all lines that do not use complying inks. The plant ink and solvent usage on one particular day is as follows:

Line	Ink conc., gallons	Dilution to concentrate ratio (by vol.)	Dilution solvent
1	30	1:1	VOC
2	25	1.5:1	Water
3	55	1.5:1	VOC
4	20	1:1	Water
5	60	2:1	VOC
6	35	0.75:1	VOC

Production Lines 1, 3, 5, and 6 are controlled by refrigeration condensers. What must the daily solvent recovery be for the plant to meet RACT requirements (overall reduction in VOCs of 65 percent) if we assume all solvents are VOCs?

First, calculate the composition of the ink concentrate in volume percent. VOC volume percent is:

$$\frac{.3055\text{ lb methanol}}{\text{lb ink concentrate}} \times \frac{10.8\text{ lbs ink conc.}}{1\text{ gallon ink conc.}} \times \frac{1\text{ gallon methanol}}{6.6\text{ lbs methanol}} =$$

$$\frac{50\text{ gal methanol}}{100\text{ gal ink conc.}}\text{ or 50 percent.}$$

Pigment volume percent is 50% (as supplied from formulation data).

Since 50 percent is less than 60 percent, the ink concentrate does not meet the high solids ink criteria (ink as applied to the substrate, less water, must contain 60 percent by volume or more of nonvolatile material). The addition of dilution solvent or water can not alter this conclusion. Therefore, all the as used ink does not comply with the high solids criteria.

Now, check the ink formulations on Lines 2 and 4 to see if either meets the criteria for water-borne inks as discussed in Examples 1 and 2 of Section 2.

LINE 2

The dilution to concentrate ratio is 1.5 gallons water to 1 gallon ink concentrate.

The volume percent VOC is

$$\frac{10.8 \text{ lb ink conc.}}{\text{gal ink conc.}} \times \frac{0.3055 \text{ lb methanol}}{1 \text{ lb ink conc.}} \times \frac{1 \text{ gal methanol}}{6.6 \text{ lb methanol}}$$

$$= \frac{0.5 \text{ gal methanol}}{\text{gal ink conc.}}$$

Volatile content = 1.5 gal water + 0.5 gal methanol
= 2.0 gal

The VOC content of the volatile portion is

$$\frac{0.5 \text{ gal VOC}}{2.0 \text{ gal volatile material}} = 0.25$$

This is a complying water-based ink. The VOC from this ink is therefore exempt from the 65 percent control requirement.

$$\text{VOC exempt} = \frac{12.5 \text{ gal VOC}}{\text{day}} \times \frac{6.6 \text{ lb VOC}}{\text{gal VOC}} = \frac{82.5 \text{ lb VOC}}{\text{day}}$$

LINE 4

The dilution to concentrate ratio is 1 gallon water to 1 gallon ink concentrate. From Line 2, we know that there is 0.5 gallon methanol per one gallon of ink concentrate.

Volatile content = 1.0 gal water + 0.5 gal methanol = 1.5 gal

VOC content of volatile portion is

$$\frac{0.5 \text{ gal VOC}}{1.5 \text{ gal volatile material}} = 0.33$$

The VOC content of the volatile portion of the water-borne ink must not exceed 25 percent to comply with the regulations. Therefore, Line 4 is not in compliance with the regulations.

Then, calculate the gallons of VOC used per line that contribute to the baseline uncontrolled VOC emissions, i.e., Lines 1, 3, 4, 5, and 6:

Line	VOC from ink conc., gal	Dilution VOC, gal	Total, gal
1	15	30	45
3	27.5	82.5	110
4	10	0	10
5	30	120	150
6	17.5	26.25	43.75
			358.75

The daily uncontrolled emissions by weight that are subject to the control requirement are

$$358.75 \text{ gal VOC} \times \frac{6.6 \text{ lb VOC}}{1 \text{ gal VOC}} = 2367.75 \text{ lb VOC}$$

The daily solvent recovery by refrigeration must be:

$$2367.75 \text{ lb} \times 0.65 = 1539 \text{ lb VOC.}$$

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SECTION 6

COMPLEX CALCULATIONS

This section includes two problems which demonstrate complex situations. To solve these problems, several factors must be considered and a series of calculations must be completed. Example 1 presents a packaging rotogravure printer which uses five inks on four presses. The inks are used in different proportions on each press. The problem incorporates a variety of compliance methods. The problem asks if the plant is in compliance with a source specific SIP revision allowing a daily bubble calculation and a VOC emission reduction requirement of 65 percent from noncomplying inks. Example 2 presents a publication rotogravure facility which uses various inks on three presses. Ink data are provided. The problem asks if the plant is in compliance with the state SIP that allows a daily bubble calculation and a VOC emission reduction requirement of 75 percent from noncomplying inks. Unless otherwise indicated, all solvents are considered to be VOCs.

Example 1 -

A packaging rotogravure printing operation has four presses using the same five inks, though in different proportions at each press. The density of water is 8.33 lb/gal. The ink compositions as applied from Reference Method 24 testing and supplied manufacturers' data are as follows:

Ink	Composition, vol %			Ink density, lb/gal	VOC* density, lb/gal
	Solids	VOC	Water		
A	65.0	35.0	0.0	11.85	6.0
B	20.0	27.0	53.0	9.30	6.5
C	10.0	22.0	68.0	8.60	6.5
D	7.5	90.0	2.5	6.91	6.2
E	10.5	89.5	0.0	6.95	6.0

*From formulation and dilution data for press ready ink.

In a given 24-hour period, ink usage for the four presses is as follows:

Press	Ink usage, gallons/day A	B	C	D	E
1	10	10	10	10	10
2	-	-	5	30	10
3	5	15	25	-	5
4	10	5	10	5	5

Presses 1 and 2 are controlled by catalytic afterburners that have a tested combined capture and destruction efficiency of 80.0 percent for each line. Presses 3 and 4 are uncontrolled. Is the plant in compliance with a source specific SIP revision allowing a daily bubble calculation to determine the difference in allowable versus actual emissions for credit purposes from complying inks and a VOC emission reduction requirement of 65 percent from noncomplying inks?

Actual VOC emissions must be compared to allowable VOC emissions to determine compliance. Inks A and C are complying inks; A is a high solids ink that contains at least 60 percent by volume, less water, nonvolatile material, and C is a water-borne ink whose volatile fraction is at least 75 percent by volume water and not more than 25 percent by volume VOC. In calculating the allowable emissions for this source, the VOC emissions from inks that exactly meet the high solids and water-borne criteria are included because the facility receives credit for the difference in allowable versus total actual emissions according to the SIP.

ACTUAL VOC EMISSIONS

I. Press 1

Ink A

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.350 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{21.0 \text{ lb VOC}}{\text{day}}$$

Ink B

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.270 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{17.6 \text{ lb VOC}}{\text{day}}$$

Ink C

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.220 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{14.3 \text{ lb VOC}}{\text{day}}$$

Ink D

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.900 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.2 \text{ lb VOC}}{\text{gal VOC}} = \frac{55.8 \text{ lb VOC}}{\text{day}}$$

Ink E

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.895 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{53.7 \text{ lb VOC}}{\text{day}}$$

Press 1 is controlled by a catalytic afterburner with an overall control efficiency of 80 percent. Actual VOC emissions from Press 1 are

[21.0 + 17.6 + 14.3 + 55.8 + 53.7] (1 - 0.80) = 32.5 lb VOC/day.

II. Press 2

Ink C

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.220 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{7.2 \text{ lb VOC}}{\text{day}}$$

Ink D

$$\frac{30 \text{ gal ink}}{\text{day}} \times \frac{0.900 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.2 \text{ lb VOC}}{\text{gal VOC}} = \frac{167.4 \text{ lb VOC}}{\text{day}}$$

Ink E

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.895 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{53.7 \text{ lb VOC}}{\text{day}}$$

Press 2 is controlled by a catalytic afterburner with an overall control efficiency of 80 percent. Actual VOC emissions from Press 2 are

[7.2 + 167.4 + 53.7](1 - 0.80) = 45.7 lb VOC/day.

III. Press 3

Ink A

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.350 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{10.5 \text{ lb VOC}}{\text{day}}$$

Ink B

$$\frac{15 \text{ gal ink}}{\text{day}} \times \frac{0.270 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{26.3 \text{ lb VOC}}{\text{day}}$$

Ink C

$$\frac{25 \text{ gal ink}}{\text{day}} \times \frac{0.220 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{35.8 \text{ lb VOC}}{\text{day}}$$

Ink E

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.895 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{26.9 \text{ lb VOC}}{\text{day}}$$

Emissions from Press 3 are uncontrolled. Actual VOC emissions are [10.5 + 26.3 + 35.8 + 26.9] = 99.5 lb VOC/day.

IV. Press 4

Ink A

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.350 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{21.0 \text{ lb VOC}}{\text{day}}$$

Ink B

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.270 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{8.8 \text{ lb VOC}}{\text{day}}$$

Ink C

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.220 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{14.3 \text{ lb VOC}}{\text{day}}$$

Ink D

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.900 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.2 \text{ lb VOC}}{\text{gal VOC}} = \frac{27.9 \text{ lb VOC}}{\text{day}}$$

Ink E

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.895 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{26.9 \text{ lb VOC}}{\text{day}}$$

Emissions from Press 4 are uncontrolled. Actual VOC emissions are [21.0 + 8.8 + 14.3 + 27.9 + 26.9] = 98.9 lb VOC/day.

Actual VOC emissions from all four presses are [32.5 + 45.7 + 99.5 + 98.9] = 276.6 lb VOC/day.

ALLOWABLE VOC EMISSIONS

For this problem, allowable emissions for complying inks are determined by calculating the gallons of ink used per day based on solids volume percent of the ink and the allowed solids volume percent of the complying formulation. By assuming that the VOC densities are the same, the allowable VOC emissions can be calculated.

I. Press 1

Ink A: This ink is a high solids ink (65 volume percent) with 35 volume percent VOC and no water. A complying ink will apply the same amount of solids but will contain a solids volume percent of 60. The gallons of solids applied are

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.65 \text{ gal solids}}{\text{gal ink}} = \frac{6.5 \text{ gal solids}}{\text{day}}$$

The amount of ink used with an exactly complying formulation applying the same amount of solids would be

$$\frac{6.5 \text{ gal solids}}{\text{day}} \times \frac{1 \text{ gal ink}}{0.60 \text{ gal solids}} = \frac{10.83 \text{ gal ink}}{\text{day}}$$

Assuming the VOC solvent density is the same, the allowable VOC emissions are

$$\frac{10.83 \text{ gal ink}}{\text{day}} \times \frac{0.40 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{26.0 \text{ lb VOC}}{\text{day}}$$

Ink B: This ink is a water-borne ink (53.0 volume percent) with 27.0 volume percent VOC and 20.0 volume percent solids.

Uncontrolled emissions are 17.6 lb VOC/day.

Allowable VOC emissions are (17.6 lb VOC/day)(1 - 0.65) = 6.2 lb VOC/day.

Ink C: This ink is a water-borne ink (68.0 volume percent) with 22.0 volume percent VOC and 10.0 volume percent solids. A complying ink will contain the same volumetric amount of solids; hence, the amount of ink used is the same. However, the complying ink can have a higher VOC content as follows:

Volatile portion = 1.0 - 0.1 = 0.90

VOC content = 0.25 x 0.90 = 0.225

Assuming the VOC density is the same, the allowable VOC emissions from the complying ink are

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.225 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{14.6 \text{ lb VOC}}{\text{day}}$$

Ink D: This ink is a solvent-based ink (90.0 volume percent) with 2.5 volume percent water and 7.5 volume percent solids.

Uncontrolled emissions are 55.8 lb VOC/day.

Allowable emissions are (55.8 lb VOC/day)(1 - 0.65) = 19.5 lb VOC/day.

Ink E: This ink is a solvent-based ink (89.5 volume percent) with 10.5 volume percent solids and no water.

Uncontrolled emissions are 53.7 lb VOC/day.

Allowable emissions are (53.7 lb VOC/day)(1 - 0.65) = 18.8 lb VOC/day.

Allowable VOC emissions from Press 1 are (26.0 + 6.2 + 14.6 + 19.5 + 18.8) = 85.1 lb VOC/day.

II. Press 2

Ink C: The amount of ink used is the same, but the VOC content is higher (22.5 volume percent). Assuming the same VOC density, the VOC emissions from the complying ink are

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.225 \text{ gal VOC}}{\text{day}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{7.3 \text{ lb VOC}}{\text{day}}$$

Ink D

Uncontrolled emissions are 167.4 lb VOC/day.

Allowable emissions are (167.4 lb VOC/day)(1 - 0.65) = 58.6 lb VOC/day.

Ink E

Uncontrolled emissions are 53.7 lb VOC/day.

Allowable emissions are (53.7 lb VOC/day)(1 - 0.65) = 18.8 lb VOC/day.

Allowable VOC emissions from Press 2 are (7.3 + 58.6 + 18.8) = 84.7 lb VOC/day.

III. Press 3

Ink A: A complying ink will apply the same amount of solids but will contain a solids volume percent of 60. The gallons of solids applied are

$$\frac{5 \text{ gal ink}}{\text{day}} \times \frac{0.65 \text{ gal solids}}{\text{gal ink}} = \frac{3.25 \text{ gal solids}}{\text{day}}$$

The amount of ink used with a complying formulation is

$$\frac{3.25 \text{ gal solids}}{\text{day}} \times \frac{1 \text{ gal ink}}{0.60 \text{ gal solids}} = \frac{5.4 \text{ gal ink}}{\text{day}}$$

Assuming the VOC density is the same, the allowable VOC emissions are

$$\frac{5.4 \text{ gal ink}}{\text{day}} \times \frac{0.40 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{13.0 \text{ lb VOC}}{\text{day}}$$

Ink B

Uncontrolled emissions are 26.3 lb VOC/day.

Allowable emissions are (26.3 lb VOC/day)(1 - 0.65) = 9.2 lb VOC/day.

Ink C: The amount of ink used is the same, but the VOC content is higher (22.5 volume percent). Assuming the same VOC density, the VOC emissions from the complying ink are

$$\frac{25 \text{ gal ink}}{\text{day}} \times \frac{0.225 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal VOC}} = \frac{36.6 \text{ lb VOC}}{\text{day}}$$

Ink E

Uncontrolled emissions are 26.9 lb VOC/day.

Allowable emissions are (26.9 lb VOC/day)(1 - 0.65) = 9.4 lb VOC/day.

Allowable VOC emissions from Press 3 are (13.0 + 9.2 + 36.6 + 9.4) = 68.2 lb VOC/day.

IV. Press 4

Ink A: A complying ink will apply the same amount of solids but will contain a solids volume percent of 60. The gallons of solids applied are

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.65 \text{ gal solids}}{\text{gal ink}} = \frac{6.5 \text{ gal solids}}{\text{day}}$$

The amount of complying ink used is

$$\frac{6.5 \text{ gal solids}}{\text{day}} \times \frac{1 \text{ gal ink}}{0.60 \text{ gal solids}} = \frac{10.83 \text{ gal ink}}{\text{day}}$$

With the same VOC, the allowable VOC emissions are

$$\frac{10.83 \text{ gal ink}}{\text{day}} \times \frac{0.40 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{26.0 \text{ lb VOC}}{\text{day}}$$

Ink B

Uncontrolled emissions are 8.8 lb VOC/day.

Allowable emissions are (8.8 lb VOC/day)(1 - 0.65) = 3.1 lb VOC/day.

Ink C: The amount of ink used is the same, but the VOC content is higher (22.5 volume percent). Assuming the same VOC solvent density, the VOC emissions from the complying ink are

$$\frac{10 \text{ gal ink}}{\text{day}} \times \frac{0.225 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.5 \text{ lb VOC}}{\text{gal ink}} = \frac{14.6 \text{ lb VOC}}{\text{day}}$$

Ink D

Uncontrolled emissions are 27.9 lb VOC/day.

Allowable emissions are (27.9 lb VOC/day)(1 - 0.65) = 9.8 lb VOC/day.

Ink E

Uncontrolled emissions are 26.9 lb VOC/day.

Allowable emissions are (26.9 lb VOC/day)(1 - 0.65) = 9.4 lb VOC/day.

Allowable VOC emissions from Press 4 are [26.0 + 3.1 + 14.6 + 9.8 + 9.4] = 62.9 lb VOC/day.

Allowable VOC emissions from all four presses are

[85.1 + 84.7 + 68.2 + 62.9] = 300.9 lb VOC/day.

Compare total actual VOC emissions to total allowable VOC emissions to determine compliance under the bubble.

Press	Actual VOC emissions, lb/day	Allowable VOC emissions, lb/day
1	32.5	85.1
2	45.7	84.7
3	99.5	68.2
4	98.9	62.9
Total	276.6	300.9

Since the total allowable VOC emissions are greater than the total actual VOC emissions for this day, the plant is in compliance.

- -

Example 2 -

A publication rotogravure facility has three presses. One press uses four high VOC inks and has a carbon adsorber with a tested combined capture and recovery efficiency of 78.0 percent. A second press uses two water-borne inks and a high VOC ink. A third press uses five water-borne inks. The second and third presses are uncontrolled. The volumes of inks used in a 24-hour period and the ink compositions from Reference Method 24A testing and manufacturer's data are as follows:

Press No.	Label	Amount used, gal/day	Composition, Vol. %			Ink density, lb/gal	Ink VOC density, lb/gal*
			Solids	VOC	Water		
1	A	20	5.0	95.0	0.0	7.21	6.8
	B	20	10.0	90.0	0.0	7.98	7.2
	C	20	7.0	93.0	0.0	7.10	6.5
	D	20	8.0	92.0	0.0	7.64	7.0
2	E	40	15.0	17.0	68.0	8.94	6.0
	F	20	10.0	27.0	63.0	8.43	6.2
	G	20	10.0	90.0	0.0	7.80	7.0
3	H	15	15.0	17.0	68.0	8.94	6.0
	I	15	15.0	21.0	64.0	8.95	6.5
	J	15	10.0	22.5	67.5	8.52	6.2
	K	15	10.0	18.0	72.0	8.58	6.0
	L	15	12.0	15.0	73.0	8.83	6.3

*From formulation and dilution data for press ready ink.

Is the plant in compliance with the source specific SIP revision that allows a daily bubble calculation to determine any credit due from the difference between allowable and actual emissions for complying inks and a VOC emission reduction requirement of 75 percent from noncomplying inks?

Actual VOC emissions must be compared to allowable VOC emissions to determine compliance. Inks E, H, I, J, K, and L are complying water-based inks whose volatile fractions are at least 75 percent by volume water and not more than 25 percent by volume VOC. In calculating the allowable emissions, the VOC emissions from inks that meet the water-based criteria exactly are included so that credit may be given for the difference in allowable versus total actual emissions.

The calculations of actual and allowable VOC emissions are performed for Inks A, F, and H to illustrate the procedure.

ACTUAL VOC EMISSIONS

Ink A: Uncontrolled emissions are

$$\frac{20 \text{ gal ink}}{\text{day}} \times \frac{0.95 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.8 \text{ lb VOC}}{\text{gal VOC}} = \frac{129.2 \text{ lb VOC}}{\text{day}}$$

The emissions are controlled by a carbon adsorber with an overall control efficiency of 78 percent. Actual emissions are

$$\frac{129.2 \text{ lb VOC}}{\text{day}} \times (1 - 0.78) = \frac{28.4 \text{ lb VOC}}{\text{day}}$$

Ink F: Uncontrolled emissions are

$$\frac{20 \text{ gal ink}}{\text{day}} \times \frac{0.27 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.2 \text{ lb VOC}}{\text{gal VOC}} = \frac{33.5 \text{ lb VOC}}{\text{day}}$$

Since this press is uncontrolled, actual emissions are 33.5 lb VOC/day.

Ink H: Uncontrolled emissions are

$$\frac{15 \text{ gal ink}}{\text{day}} \times \frac{0.17 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{15.3 \text{ lb VOC}}{\text{day}}$$

Since this press is uncontrolled, actual emissions are 15.3 lb VOC/day.

ALLOWABLE VOC EMISSIONS

Ink A: Uncontrolled emissions are 129.2 lb VOC/day. Required control is 75 percent. Allowable emissions are

$$\frac{129.2 \text{ lb VOC}}{\text{day}} \times (1 - 0.75) = \frac{32.3 \text{ lb VOC}}{\text{day}}$$

Ink F: Uncontrolled emissions are 33.5 lb VOC/day. Required control is 75 percent.

Assuming the VOC solvent density is the same for the two inks, the allowable VOC emissions from this ink are

$$\frac{33.5 \text{ lb VOC}}{\text{day}} \times (1 - 0.75) = \frac{8.4 \text{ lb VOC}}{\text{day}}$$

Ink H: A complying water-based ink will contain the same volumetric amount of solids; hence, the amount of ink used remains the same. However, the complying ink will have a different allowable VOC content as follows;

Volatile portion = 1 - 0.15 = 0.85.

VOC content = 0.25 x 0.85 = 0.213.

Assuming the VOC density is the same, the allowable VOC emissions from the complying ink are

$$\frac{15 \text{ gal ink}}{\text{day}} \times \frac{0.213 \text{ gal VOC}}{\text{gal ink}} \times \frac{6.0 \text{ lb VOC}}{\text{gal VOC}} = \frac{19.2 \text{ lb VOC}}{\text{day}}$$

The calculations for all inks are summarized in the following table.

Press no.	Ink label	Amount of ink used, gal/day	Ink VOC content, vol. frac.	VOC density, lb/gal	Overall control eff., %	Actual VOC emissions, lb/day	Required VOC reduction, %	Complying ink VOC content, vol. frac.	Allowable VOC emissions, lb/day
1	A	20	0.95	6.8	78	28.4	75	-	32.3
1	B	20	0.90	7.2	78	28.5	75	-	32.4
1	C	20	0.93	6.5	78	26.6	75	-	30.2
1	D	20	0.92	7.0	78	28.3	75	-	32.2
2	E	40	0.17	6.0	-	40.8	-	0.213	51.1
2	F	20	0.27	6.2	-	33.5	75	-	8.4
2	G	20	0.90	7.0	-	126.0	75	-	31.5
3	H	15	0.17	6.0	-	15.3	-	0.213	19.2
3	I	15	0.21	6.5	-	20.5	-	0.213	20.8
3	J	15	0.225	6.2	-	20.9	-	0.225	20.9
3	K	15	0.18	6.0	-	16.2	-	0.225	20.3
3	L	15	0.15	6.3	-	14.2	-	0.220	20.8
						399.2			320.1

Since actual VOC emissions are greater than allowable VOC emissions, the facility is not in compliance.

SECTION 7

ALTERNATE EMISSION LIMIT

The U.S. EPA has developed an alternate emission limit applicable to flexographic printing and packaging rotogravure printing presses which is available to graphic arts sources through a SIP revision (See Appendix C). It is particularly useful in emission trading calculations. The alternate emission limit of 0.5 pound of volatile organic compounds (VOC) per pound of solids in the ink is essentially equivalent to the RACT limits recommended in the CTG. The 0.5 lb VOC/lb solids limit includes all VOC added to the ink: VOC in the purchased ink, VOC added to cut the ink to achieve desired press viscosity, and VOC added to ink on the press to maintain viscosity during the press run.

The following three examples show basic procedures for calculating emissions using this proposed standard.

Example 1 -

A flexographic printer uses one gallon of an ink formulation on a press with the following characteristics:

total VOC content	= 25 weight percent	(includes all additions)
solids content	= 55 weight percent	
water content	= 20 weight percent	

Does the printer comply with the 0.5 lb VOC per lb solids regulation?

$$\frac{\text{lb VOC}}{\text{lb solids}} = \frac{0.25 \text{ lb VOC}}{\text{lb ink}} \div \frac{0.55 \text{ lb solids}}{\text{lb ink}}$$

$$= \frac{0.45 \text{ lb VOC}}{\text{lb solids}}$$

Since 0.45 lb VOC/lb solids is less than 0.5 lb VOC/lb solids, the printer is in compliance.

Example 2 -

A packaging rotogravure printer uses an ink formulation on two presses with the following characteristics per gallon of ink:

Press A

total VOC content of ink	= 0.25 lb/lb ink (press ready)
solids content of ink	= 0.50 lb/lb ink
water content of ink	= 0.25 lb/lb ink
dilution solvent added	= 0.20 lb/lb ink

Press B

total VOC content of ink	= 0.15 lb/lb ink
solids content of ink	= 0.55 lb/lb ink
water content of ink	= 0.30 lb/lb ink
solvent added during press run	= 0.10 lb/lb ink

Determine the compliance status of each press. This simple example demonstrates the concept. In a real case, several inks with varying compositions would be encountered.

Press A

The total amount of VOC used is

0.25 lb VOC/lb ink + 0.20 lb VOC/lb ink = 0.45 lb VOC/lb ink

$$\frac{\text{lb VOC}}{\text{lb solids}} = \frac{0.45 \text{ lb VOC}}{0.50 \text{ lb solids}} = 0.90$$

Since 0.90 lb VOC/lb solids is greater than 0.50 lb VOC/lb solids, Press A is not in compliance.

Press B

The total amount of VOC used is

0.15 lb VOC/lb ink + 0.10 lb VOC/lb ink = 0.25 lb VOC/lb ink

$$\frac{\text{lb VOC}}{\text{lb solids}} = \frac{0.25 \text{ lb VOC}}{0.55 \text{ lb solids}} = 0.45$$

Therefore, Press B is in compliance.

Example 3 -

A flexographic printer operates four presses. The printer wishes to comply with the 0.5 lb VOC per lb solids regulation by bubbling the plant's emissions on a 24-hour basis. The following table summarizes the printer's formulations and ink and VOC amounts used on the four presses for the 24-hour compliance period. The dilution solvents are 100 percent VOC. Does the printer meet the regulatory emission limit based on a source specific SIP revision allowing the bubble calculation?

Press	VOC content of ink, wt. %	Solids content of ink, wt. %	Water content of ink, wt. %	Ink quantity used, gal	Dilution solvent A addition, gal	Dilution solvent B addition, gal
A	10	70	20	15	-	-
B	50	50	-	20	10	0
C	15	25	60	30	5	10
D	-	80	20	15	-	5
Total				80	15	15

The following densities apply:

Ink - 7.40 lb/gal
Dilution solvent A - 6.30 lb/gal
Dilution solvent B - 7.10 lb/gal

The first step in solving this problem is to calculate the total amounts of VOC and solids used at the facility as follows:

Press A

$$\text{Total VOC} = \left(\frac{0.10\text{ lb VOC}}{\text{lb ink}}\right)\left(\frac{7.40\text{ lb ink}}{\text{gal ink}}\right)(15\text{ gal ink})$$

$$= 11.1\text{ lb VOC}$$

$$\text{Total solids} = \left(\frac{0.70\text{ lb solids}}{\text{lb ink}}\right)\left(\frac{7.40\text{ lb ink}}{\text{gal ink}}\right)(15\text{ gal ink})$$

$$= 77.7\text{ lb solids}$$

Press B

$$\text{Total VOC} = \left(\frac{0.50 \text{ lb VOC}}{\text{lb ink}}\right)\left(\frac{7.40 \text{ lb ink}}{\text{gal ink}}\right)(20 \text{ gal ink})$$

$$+ (10 \text{ gal dilution solvent})\left(\frac{6.30\text{lb VOC}}{\text{gal dilution solvent}}\right)$$

$$= 137 \text{ lb VOC}$$

$$\text{Total solids} = \left(\frac{0.50 \text{ lb solids}}{\text{lb ink}}\right)\left(\frac{7.40 \text{ lb ink}}{\text{gal ink}}\right)(20 \text{ gal ink})$$

$$= 74 \text{ lb solids}$$

Press C

$$\text{Total VOC} = \left(\frac{0.15 \text{ lb VOC}}{\text{lb ink}}\right)\left(\frac{7.40 \text{ lb ink}}{\text{gal ink}}\right)(30 \text{ gal ink})$$

$$+ (5 \text{ gal dilution solvent})\left(\frac{6.30 \text{ lb VOC}}{\text{gal dilution solvent}}\right)$$

$$+ (10 \text{ gal dilution solvent})\left(\frac{7.10 \text{ lb VOC}}{\text{gal dilution solvent}}\right)$$

$$= 135.8 \text{ lb VOC}$$

$$\text{Total solids} = \left(\frac{0.25 \text{ lb solids}}{\text{lb ink}}\right)\left(\frac{7.40 \text{ lb ink}}{\text{gal ink}}\right)(30 \text{ gal ink})$$

$$= 55.5 \text{ lb VOC}$$

Press D

$$\text{Total VOC} = \left(\frac{5 \text{ gal dilution solvent}}{\text{lb solids}}\right)\left(\frac{7.10 \text{ lb VOC}}{\text{gal dilution solvent}}\right)$$

$$= 35.5 \text{ lb VOC}$$

$$\text{Total solids} = \left(\frac{0.80 \text{ lb solids}}{\text{lb ink}}\right)\left(\frac{7.40 \text{ lb ink}}{\text{gal ink}}\right)(15 \text{ gal ink})$$

$$= 88.8 \text{ lb solids}$$

Total VOC emitted from the four presses at the facility during the 24-hour compliance period is:

$$11.1 \text{ lb} + 137 \text{ lb} + 135.8 \text{ lb} + 35.5 \text{ lb} = 319.4 \text{ lb VOC}$$

Total solids applied on the four presses at the facility during the 24-hour compliance period are:

77.7 lb + 74 lb + 55.5 lb + 88.8 lb = 296 lb solids

Finally, the pound of VOC per pound of solids is calculated as follows:

$$\frac{\text{lb VOC}}{\text{lb solids}} = \frac{319.4 \text{ lb VOC}}{296 \text{ lb solids}} = \frac{1.08 \text{ lb VOC}}{\text{lb solids}}$$

Therefore, the facility does not meet the emission limit by bubbling its emissions over a 24-hour compliance period.

APPENDIX A

PROCEDURES FOR CERTIFYING QUANTITY OF VOLATILE ORGANIC COMPOUNDS EMITTED BY PAINT, INK, AND OTHER COATINGS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/:
December

Air

EPA

Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings

Note: This copy includes the two revised pages.

ESED

EPA-450/3-84-019

Procedure for Certifying Quantity of Volatile Organic Compounds Emitted By Paint, Ink, and Other Coatings

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1984

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PREFACE

This manual was conceived as a way to provide simple step-by-step instructions for certifying the quantity of volatile organic compounds (VOC) that will be released by a coating. It has not turned out that way. The guidance is here, but in spite of great diligence, the instructions remain imposing.

The manual was prepared for several reasons. First, the coatings industry, as represented by the National Paint and Coatings Association, had requested a certification procedure which would relieve their customers the expense of analysis. Second, the complexity of the calculations necessary to determine compliance, for example, when dilution solvent is added to a coating, continue to confound Federal, State and Local enforcement personnel. Finally, results of a recent review of the Agency's reference method for determining VOC reemphasized the importance of analytical procedures to verify VOC content.

In response to the results of the review of the test methods, this manual reaffirms that Reference Method 24 or its constituent methods developed by the American Society for Testing and Materials (ASTM), are the procedures by which the VOC content of a coating will be determined for compliance with Federal regulations. The earliest guidance was not so specific. In 1977, the first report[1], written to assist States in developing regulations for sources of VOC emissions, provided recommendations for the maximum allowable VOC content for complying coatings in a variety of industries. These values were expressed in mass of VOC per unit volume of coating. In deriving the recommended limitation, the VOC content of a coating was calculated based on the solids content provided by the coating manufacturer. The Agency calculated the mass of VOC in the coating by assuming the VOC had a density of 7.36 pounds per gallon.

Solvent and VOC were used somewhat interchangebly even though it was recognized that organics such as resin monomer, oligimers, and reaction by-products could be released by a coating during the cure. There was no accepted analytical method available for measuring the total VOC which would be released by a coating. The initial guidance[1] provided an analytical method for use only for air-dry coatings, those where all VOC emissions would be expected to come as a result of evaporation of solvent. On a volume basis, air dry coatings constituted the largest catagory of coatings then in use.

The Agency subsequently developed a more general analytical procedure that could be used to determine the total VOC in a coating. On October 3, 1980, the Agency published "Reference Method 24 (RM-24) -

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[1]Control of Volatile Organic Emissions from Stationary Sources - Volume II: Surface Caoting of Cans, Coils, Paper, Fabrics, Automobiles, and Light-duty Trucks, Document No. EPA-450/2-77-008.

Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings," in the Federal Register (45 FR 65958). For the first time the Agency formally specified an analytical method for the VOC content of those coatings that cure by chemical reaction. Even then, the announcement continued to allow the manufacturer's formulation to be used to calculate the VOC content but specified that the analytical technique, RM-24, would be the reference in any conflict between the two.

During 1981 and 1982, as more State and Federal regulations were established, the demand for low-solvent coatings began a continuing increase in the sales volume of reaction-cure coatings. There was some concern voiced by the industry in how appropriate the reference method was for these type coatings. To find out, the Agency began a review of RM-24 to determine the effect of temperature and exposure time on the indicated VOC "content". It was concluded that the maximum effect of those time-temperature combinations that were examined amounted to only about a 10 percent variation. Somewhat more surprising was that the solvent sometimes accounted for only 50 to 70 percent of the total VOC measured by the reference method.

The obvious conclusion was that RM-24 is a better measure of the total organics freed by a coating than is the solvent. This manual implements a policy based on that conclusion. Certification of VOC content on the attached Data Sheets must be based on an analysis using RM-24. No longer will solvent content be permitted as a surrogate for VOC unless a showing is first made that its use is a reasonable alternative or equivalent method of determining the VOC content of that particular coating.

One final comment. Since VOC is not always synonomous with solvent, it follows that the amount of solids in a coating cannot be obtained by subtracting the solvent from the total volume of coating. The original Federal Register proposal for RM-24, published on October 3, 1980, recommended the American Society of Test Materials test Number D2697 as the appropriate method for determining solids content. Subsequent comments from the industry maintained that this test is unreliable. As a result, when promulgated in 1980, RM-24 specified that the solids content of a coating can be obtained only from the manufacturer's formulation of the coating.

Dennis Crumpler

Dennis Crumpler
December 14, 1984

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GLOSSARY OF TERMS

"As Applied"	the condition of a coating after dilution by the user just prior to application to the substrate.
"As Supplied"	the condition of a coating before dilution, as sold and delivered by the coating manufacturer to the user.
$(D_c)_a$	coating density "as applied"
$(D_c)_s$	coating density, "as supplied"
D_d	density of dilution solvent
$D_d^{\dagger}$	density of organic solvent/water mixture
D_w	density of water (8.33 lb/gal)
R_d	dilution solvent ratio, equals the volume of VOC added per unit volume of coating "as supplied"
$R_d^{\dagger}$	equals the volume of premixed water and VOC added per unit volume of coating "as supplied"
$(V_n)_a$	Volume percent solids of coating "as applied"
$(V_n)_s$	Volume percent solids of coating "as supplied"
$(VOC)_a$	VOC content of "as applied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(VOC)_s$	VOC content of "as supplied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(V_w)_a$	the water content, in volume percent, of coating "as applied"
$(V_w)_d$	the water content, in volume percent, of the dilution solvent added to the "as supplied" coating
$(V_w)_s$	the water content, in volume percent, of the coating "as supplied"
$(W_o)_a$	the organic volatile content, in weight percent, of the coating "as applied"
$(W_o)_s$	the organic volatile content, in weight percent, of the coating "as supplied"

$(W_v)_a$ — the weight percent of total volatiles in the coating "as applied"

$(W_v)_s$ — the weight percent of total volatiles in the coating "as supplied"

$(W_w)_a$ — the weight percent water in the coating "as applied"

$(W_w)_d$ — the weight percent water in the dilution solvent

$(W_w)_s$ — the weight percent water in the coating "as supplied"

1. INTRODUCTION

This Manual provides step-by-step instruction for preparation of two data sheets developed by the Environmental Protection Agency which may be used by coating manufacturers and users to present information on the quantity of volatile organic compounds* (VOC) emitted from a coating. One of the data sheets may be prepared by the manufacturer of the coating; the second would be used by the company that applies the coating to a substrate.

The first VOC data sheet, which would be prepared by the manufacturer, provides information on the volatile organic content of a coating as it is delivered to a customer. This is referred to as the VOC content of the coating "as supplied" (by the manufacturer to the user).

The second VOC data sheet, which would be prepared by the user or coater, provides information on the quantity of volatile organic compounds present as the coating is used or applied to the substrate and includes the effect of any dilution solvent added before application. This is referred to as the VOC content of the coating "as applied" (to the substrate).

The coating user may submit, and the Agency enforcing a regulation may accept, these data sheets as prima facie evidence of the actual VOC content of a coating. The referee method for ultimate determination of compliance, however, will continue to be the method specified in the applicable regulation (for example, EPA Reference Method 24 or individual ASTM methods).

*Volatile Organic Compound (VOC) - Any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method, or by procedures specified under any regulation.

2. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS SUPPLIED" BY THE COATING MANUFACTURER TO THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS SUPPLIED" BY THE MANUFACTURER

Coating Manufacturer: ______________________

Coating Identification: ______________________

Batch Identification: ______________________

Supplied To: ______________________

Properties of the coating as supplied[1] to the customer:

A. Coating Density $(D_c)_s$: ________ lb/gal ________ kg/l

/_/ ASTM D1475 /_/ Other[2]

B. Total Volatiles $(W_v)_s$: ________ Weight Percent

/_/ ASTM D2369 /_/ Other[2]

C. Water Content: 1. $(W_w)_s$ ________ Weight Percent

/_/ ASTM D3792 /_/ ASTM D4017 /_/ Other[2]

2. $(V_w)_s$ ________ Volume Percent

/_/ Calculated /_/ Other[2]

D. Organic Volatiles $(W_o)_s$: ________ Weight Percent

E. Nonvolatiles Content $(V_n)_s$: ________ Volume Percent

F. VOC Content $(VOC)_s$: 1. ________ lb/gal coating less water

or ________ kg/l coating less water

2. ________ lb/gal solids

or ________ kg/l solids

Remarks: (use reverse side)

[1]The subscript "s" denotes each value is for the coating "as supplied" by the manufacturer.

[2]Explain the other method used under "Remarks".

Signed: ______________________ Date ________

2.2 IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS SUPPLIED" COATING

This DATA SHEET is normally completed by the coating manufacturer and provided to the user.[1] It will henceforth be referred to as the "AS SUPPLIED" VOC DATA SHEET.

A. The "as supplied" coating density, $(D_c)_s$[2], is determined using "ASTM D1475 - Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in a coating, $(W_v)_s$, is determined by "ASTM D2369 - 81 Standard Method for Volatile Content of Coatings." drying conditions to be used are 110°C for 1 hour[3].

C. Water Content

1. The weight percent water, $(W_w)_s$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method."[3,4] An acceptable alternative to these procedures for purposes of preparing the data sheet would be to calculate the weight percent water from the manufacturer's coating formulation.

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[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "s" denotes those parameters of a coating when measured in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes a specified method does not give results that are representative of the actual cure mechanism, he may petition the enforcement authority for approval of an alternate analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and Federal enforcement agency.

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation should be treated in the same manner as water. The weight percent of negligibly reactive compounds in a coating should be determined from the manufacturer's formulation. The volume percent can then be calculated using equation II-1 when the weight percent and density of the negligibly reactive compounds are substituted for those of water. The weight and volume percent can be used in Equations II-2 and II-6, respectively, in place of $(W_w)_s$ and $(V_w)_s$.

2. The water content, in volume percent, $(V_w)_s$, can be calculated by the equation:

$$(V_w)_s = \frac{(W_w)_s(D_c)_s}{D_w}, \qquad \text{II-1}$$

where D_w is the density of water, 8.33 lbs/gal.

D. The organic volatiles content, $(W_o)_s$, i.e., the VOC content expressed as a percent by weight, is determined by the following equation[5]:

$$(W_o)_s = (W_v)_s - (W_w)_s \qquad \text{II-2}$$

If the coating contains no water the weight percent of organic volatiles is equal to the weight percent of total volatiles.

In other words:

$$(W_w)_s = 0 \text{ and}$$

$$(W_o)_s = (W_v)_s \qquad \text{II-3}$$

E. The volume percent solids (nonvolatiles), $(V_n)_s$, should be derived from the coating formulation using the following equation:

$$(V_n)_s = \sum_{i=1}^{p} (V_n)_{s_i} \qquad \text{II-4}$$

where $(V_n)_{s_i}$ denotes the volume percent of each

nonvolatile component in an "as supplied" coating, and "p" is the number of nonvolatile components in that coating. (Also see Footnote 1, Pg. II-3.)

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean W_w and W_v values may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS SUPPLIED" VOC DATA SHEET.

F. The VOC content of the "as supplied" coating $(VOC)_s$ can now be calculated and thereby expressed in terms used by most State or Federal regulations.

1. The mass of VOC per unit volume of coating less water:

   a. If the coating contains no water, the equation is calculated as follows:

$$(VOC)_s = \frac{(W_o)_s \ (D_c)_s}{100\%} \qquad \text{II-5}$$

   b. If the coating contains water, Equation II-5 becomes:

$$(VOC)_s = \frac{(W_o)_s \ (D_c)_s}{100\% - (V_w)_s} \qquad \text{II-6}$$

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles). For both solvent-borne and waterborne coatings, the equation is:

$$(VOC)_s = \frac{(W_o)_s \ (D_c)_s}{(V_n)_s} \qquad \text{II-7}$$

3. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS APPLIED" TO THE SUBSTRATE BY THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS APPLIED" TO THE SUBSTRATE

Coating Manufacturer: ______________________

Coating Identification: ______________________

Batch Identification: ______________________

User: ______________________

User's Coating Identification: ______________________

Properties of the coating as applied[1] by the User:

A. Coating Density $(D_c)_a$: __________ kg/l, or __________ lb/gal

/__/ ASTM D1475 /__/ Other[2]

B. Total Volatiles $(W_v)_a$: ______________________ Weight Percen

/__/ ASTM D2369 /__/ Other[2]

C. Water Content: 1. $(W_w)_a$ ______________________ Weight Percen

/__/ ASTM D3792 /__/ ASTM D4017 /__/ Other[2]

2. $(V_w)_a$ ______________________ Volume Percen

/__/ Calculated /__/ Other[2]

D. Weighted Average Density of the dilution solvent $(D_d)^3$: __________ lb/ga

/__/ ASTM D1475 /__/ Handbook /__/ Formulation

(Continued on Reverse Side)

[1]The subscript "a" denotes each value is for the coating "as applied" to the substrate.
[2]Explain the other method used under "Remarks" on reverse side
[3]The subscript "d" denotes values are for the dilution solvent

E. Dilution Solvent Ratio (R_d): ______ $\frac{\text{gal diluent}}{(\text{gal coating})_s}$[4]

or

______ $\frac{\text{liter diluent}}{(\text{liter coating})_s}$[4]

F. Organic Volatiles Content[5] $(W_o)_a$: ______________ Weight Percent

G. Non-Volatiles Content $(V_n)_a$: ______________ Volume Percent

H. VOC Content $(VOC)_a$: 1. ____________ lb/gal of coating less water

or ____________ kg/l of coating less water

2. ____________ lb/gal solids

or ____________ kg/l solids

REMARKS:

Signed: ______________________ Date: __________

[4]The subscript "s" denotes values are for the coating "as supplied" by the manufacturer.

[5]This terminology is used to be consistent with Method 24. It refers to all photochemically reactive organic compounds emitted from the coating including reactive by-products of the cure reaction, exactly the same matter as indicated in Paragraph H, i.e., volatile organic compounds, or VOC.

3.2. IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS APPLIED" COATINGS

This DATA SHEET, henceforth referred to as the "AS APPLIED" VOC DATA SHEET, is to be completed by the company which applies a coating. It provides information on the amount of volatile organic compounds (VOC) in the coating "as applied" to the substrate by accounting for the quantity of diluent solvent added to the "as supplied" coating prior to application. If a coating is diluted only with water or a solvent of negligible photochemical reactivity, the user merely doucments the fact (see Step E.1. and also Footnote 4, Pg. III-5.). Otherwise, several avenues exist for the coater to certify the VOC content:
(1) Maintain adequate records of how much organic solvent is added to each coating and use that information and the "AS SUPPLIED" VOC DATA SHEET[2] to calculate the VOC content "as applied." In this case begin with Step D.
(2) If the "AS SUPPLIED" DATA SHEET is available, but dilution records are not, begin the "As Applied" determination with Step A, skip Steps B and C, and proceed to Step D.
(The user may choose to analyze an "As Supplied" coating using Reference Method 24 and complete the "AS SUPPLIED" VOC DATA SHEET rather than have the coating manufacturer complete it. The volume percent solids, however, will necessarily continue to be supplied by the coating manufacturer.)
(3) Analyze each diluted coating with the same method used to generate the data provided by the coating manufacturer on the "AS SUPPLIED" VOC DATA SHEET. (See Chapter 2 of this Manual.) In this case begin with Step A.[1]

A. The "as applied" coating density, $(D_c)_a$[2], is determined using "ASTM D1475-Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in the coating, $(W_v)_a$ is determined by "ASTM D2369-81 Standard Method for Volatile Content of Coatings." The drying conditions to be used are 110°C for 1 hour[3].

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[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "a" denotes those parameters of a coating in the "as applied" condition, i.e., after dilution by the user. The subscript "s" denotes the parameters of a coating in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes the specified method gives results that are not representative of the VOC released during the normal cure, he may petition the enforcement authority for approval of an alternative analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and/or Federal enforcement agency.

C. The water content is necessary only if the coating has been diluted with a mixture of organic solvent and water.[4,5] If the dilution solvent is 100 percent organic, or if the weight and volume percent water in the mixture is known, proceed directly to Step D.

The weight percent water, $(W_w)_a$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method." (Also see Footnote 3, Pg. III-4.)

The water content, in volume percent, $(V_w)_a$, can be calculated by the equation:

$$(V_w)_a = \frac{(W_w)_a \ (D_c)_a}{D_w} \qquad \text{III-1}$$

where D_w is the density of water, 8.33 lb/gal.

---

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation, should be treated in the same manner as water. The weight percent of negligibly reactive compounds in the dilution solvent must be known either from the coater's mixing records or the dilution solvent supplier's formulation. The volume percent can then be calculated using Equations III-1 or III-5 when the weight percent and density of the negligibly reactive organics are substituted for those of water. The weight and volume percent of the negligibly reactive compounds can be substituted in all equations where the weight and volume percent water, (W_w) and (V_w), respectively, are used.

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean weight percent water and total volatiles, W_w and W_v respectively, may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS APPLIED" VOC DATA SHEET.

D. If the dilution solvent consists of a single compound the density may be obtained from the literature.

If the dilution solvent is a mixture of organic compounds, the density, D_d[6], can be determined analytically via ASTM D1475, or an average density can be estimated from the solvent formulation as shown below. This estimation assumes that volumes are additive.

$$D_d = \frac{100\%}{\sum_{j=1}^{m} \frac{W_j}{D_j}} \qquad \text{III-2}$$

or

$$= \frac{1}{100\%} \sum_{j=1}^{m} V_j D_j \qquad \text{III-3}$$

where: D_j, W_j, and V_j denote the density, weight percent, and volume percent of each solvent in the dilution solvent mixture and "m" is the number of organic solvents in the dilution solvent mixture.

If the dilution solvent is a mixture of photochemically reactive organics and water, the coater must know the weight percent, $(W_w)_d$, or volume percent, $(V_w)_d$, of water from his mixing records or the supplier's formulation, or he must analytically determine the weight fraction of water in the dilution solvent using ASTM D3792 or ASTM D4017. The density, D_d, of the dilution solvent may then be determined by analytically measuring the density of the organic solvent/water mixture, $D_d^{\dagger}$, using ASTM D1475 and adjusting it for the water content using the following equation. (See also Footnote 4, Pg. III-5.)

$$D_d = D_d^{\dagger} \frac{[100\% - (W_w)_d]}{[100\% - (V_w)_d]} \qquad \text{III-4}$$

Note: If either the weight or volume percent water in the dilution solvent is known, the other can be calculated by the equation:

$$(V_w)_d = \frac{(W_w)_d \; D_d^{\dagger}}{D_w} \qquad \text{III-5}$$

where "D_w" is the density of water.

---

[6]The subscript "d" denotes a parameter that pertains to that solvent used by the coater to dilute the "as supplied" coating.

E. The dilution solvent ratio, R_d, is defined as the volume of photochemically reactive organic solvent, (VOC), added per unit volume of "as supplied" coating. Stated mathematically,

$$R_d = \frac{\text{Volume photochemically reactive dilution solvent added}}{\text{Volume of "as supplied" coating}}$$

1. If the "as supplied" coating is subsequently diluted with water or a solvent which is of negligible photochemical reactivity, the VOC content will be unchanged from that reported on the "AS SUPPLIED" VOC DATA SHEET. This should be reported on the "AS APPLIED" VOC DATA SHEET by entering "0" for the dilution solvent ratio, R_d.

2. In the absence of adequate dilution records, R_d can be calculated from entries on the VOC DATA SHEETS by one of the following equations:

   a. When the dilution solvent consists only of VOC,

$$R_d = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)} \qquad \text{III-6}$$

   b. When the dilution solvent is a mixture of water and photochemically reactive organic solvent, Equation III-6 may be expressed as:

$$R_d^{\dagger} = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)^{\dagger}} \qquad \text{III-7}$$

where: $R_d^{\dagger}$ is the ratio of the volume of water and organic dilution solvent to the volume of "as supplied" coating to which it is added. (Also see Footnote 4, Pg. III-5.)

The dilution solvent ratio, R_d, may now be calculated from $R_d^{\dagger}$ by the following equation:

$$R_d = R_d^{\dagger} \left[1 - \frac{(V_w)_d}{100\%}\right] \qquad \text{III-8}$$

F. The organic volatile content $(W_o)_a$, i.e. the VOC content expressed as a percent by weight of the diluted coating, can now be calculated by either of two ways:

1. From analyses of the coating using the following equation:

$$(W_o)_a = (W_v)_a - (W_w)_a \qquad \text{III-9}$$

(See Footnotes 4 and 5, Pg. III-5.)

If the coating does not contain water, the weight percent of organic volatiles is equal to the weight percent of total volatiles, or

$$(W_o)_a = (W_v)_a \qquad \text{III-10}$$

2. By using the data from the "AS SUPPLIED" VOC DATA SHEET, the dilution solvent ratio, and the density of the dilution solvent with the following equation:

$$(W_o)_a = \frac{[(D_c)_s\ (W_o)_s/100\%] + (R_d D_d)}{(D_c)_s + (R_d D_d)} \times 100\% \qquad \text{III-11}$$

G. The volume percent solids, or nonvolatiles, $(V_n)_a$, must be calculated from the following equation where $(V_n)_s$ is obtained from the "AS SUPPLIED" VOC DATA SHEET.

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d} \qquad \text{III-12}$$

H. The VOC content of the "as applied" coating $(VOC)_a$, can now be calculated and thereby expressed in terms used in most State or Federal regulations.

1. The mass of VOC per unit volume of coating, less water, is calculated in either of two ways.

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM Methods:

(1). If the coating contains no water the equation is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\%} \qquad \text{III-13}$$

(2). If the coating contains water the following equation must be used:

$$(VOC)_a = \frac{(W_o)_a \ (D_c)_a}{100\% - (V_w)_a} \qquad \text{III-14}$$

b. Using the VOC content of the "as supplied" coating, (VOC_s), the dilution solvent ratio, and the density of the solvent, the equation is:

$$(VOC)_a = \frac{[(VOC)_s \ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{1 + R_d - (V_w)_s/100\%} \qquad \text{III-15}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles).

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM methods, the equation for both solvent-borne and waterborne coatings, is:

$$(VOC)_a = \frac{(W_o)_a \ (D_c)_a}{(V_n)_a} \qquad \text{III-16}$$

b. Using dilution information and calculation procedures only, the equation is:

$$(VOC)_a = \frac{[(VOC)_s \ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{(V_n)_s/100\%} \qquad \text{III-17}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 450/3-84-019	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings		5. REPORT DATE December 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPOR
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Air Quality Planning and Standards U. S. Environmental Protection Agency (MD-13) Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT AND PERIOD COVE
		14. SPONSORING AGENCY CODE EPA/200/04
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

This manual provides procedures by which firms may voluntarily certify the quantity of volatile organic compounds which will be emitted by a paint, ink, or other coating. Two data sheets are provided. One is to be used by the manufacturer of the coating, the other by the user. Analytical test methods and procedures for preparing the data sheets are included, as are the equations and instructions necessary to convert the analytical results into a format suitable for determining compliance with State or Federal regulations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Gro
Air Pollution Coatings Compliance Calculations Pollution Control Reference Method 24 Test Methods Volatile Organic Compounds	Air Pollution Control	13-B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 15
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

APPENDIX B

EPA REFERENCE TEST METHOD 24
EPA REFERENCE TEST METHOD 24A

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings [117]

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475–60 (Reappproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see § 60.17).[177]

2.2 ASTM D2369–81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see § 60.17).[177]

2.3 ASTM D3792–79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see § 60.17).[177]

2.4 ASTM D4017–81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see § 60.17).[177]

3. *Procedure.*

3.1 Volatile Matter Content. Use the procedure in ASTM D2369–81 (incorporated by reference—see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information: [177]

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3}$$

Eq. 24-1 [177]

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (w) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).[177]

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D1475–60 (Reapproved 1960) (incorporated by reference—see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).[177]

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.9 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For W_v and W_w run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is coaclaided that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropirate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c use the lower confidence limits, and for W_w use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \quad \text{Eq. 24-2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \quad \text{Eq. 24-3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \quad \text{Eq. 24-4}$$

Where: W_s = Weight solids, g/g.

Method 24A—Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings[169]

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

2. *Procedure.*

2.1 Weight Fraction VOC.

2.1.1 Apparatus.

2.1.1.1 Weighing Dishes. Aluminum foil, 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.

2.1.1.2 Disposable syringe, 5 ml.

2.1.1.3 Analytical Balance. To measure to within 0.1 mg.

2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of 120±2°C and an absolute pressure of 510 ±51 mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2°C for 24 hours.

2.1.1.5 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}).

Using a 5-ml syringe without a needle remove a sample of the coating. Weigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of 510 ±51 mm Hg and a temperature of 120 ±2°C for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of 120 ±2°C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475–60 (Reapproved 1980), which is incorporated by reference. It is available from the American Society of Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. It is also available for inspection at the Office of the Federal Register, Room 8401, 1100 L Street, NW., Washington, D.C. This incorporation by reference was approved by the Director of the Federal Register on November 8, 1982. This material is incorporated as it exists on the date of approval and a notice of any change in these materials will be published in the Federal Register.

2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D 1475–60 (reapproved 1980). Make a total of three determinations for each coating. Report the density $\bar{D}_o$ as the arithmetic average of the three determinations.[176]

3. *Calculations.*

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W_o using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}}$$

Equation 24A–1 [176]

Report the weight fraction VOC $\bar{W}_o$ as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content V_o using the following equation:

$$V_o = \frac{\bar{W}_o \bar{D}_c}{\bar{D}_o}$$

Equation 24A–2 [176]

4. *Bibliography.*

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475–60 (Reapproved 1980).

4.2 Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R. A., Radian Corporation. September 25, 1979. Gravure Ink Analysis.

4.3 Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation. November 5, 1979. Gravure Ink Analysis.

APPENDIX C

ALTERNATIVE COMPLIANCE FOR GRAPHIC ARTS RACT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

SEP 9 1987

MEMORANDUM

SUBJECT. Alternative Compliance for Graphic Arts RACT

FROM: Darryl D. Tyler, Director
Control Programs Development Division (MD-15)

TO: Director, Air Division, Regions I-X

As an outgrowth of comments on simplifying recordkeeping and determining compliance in the flexographic and packaging rotogravure printing industries, the Agency has decided to accept an emission limit of 0.5 lb of volatile organic compound (VOC) per pound of solids in the ink as alternative emission limit which is essentially equivalent to the reasonably available control technology (RACT) level recommended in the graphic arts control technique guideline (CTG), "Control of Volatile Organic Emissions From Existing Sources Volume VIII: Graphic Arts, Rotogravure, and Flexography," EPA-450/2-78-033, December 1978. A source-specific State implementation plan (SIP) revision for a graphic arts facility which is based on this equivalent alternative RACT emission limit will be considered valid and will be expeditiously reviewed.

Rather than applying this limit on a source-specific basis, a State may wish to revise its SIP to apply this alternative limit to all affected sources so that there will be no need for a source-specific SIP revision for each particular industrial facility. Such an approach will be acceptable to EPA.

However, States are not required to revise SIP's and adopt the 0.5 lb VOC/lb solids RACT equivalent. The EPA still considers the RACT limitations recommended in the CTG and already incorporated into most SIP's to be valid and does not propose to prohibit their use. If a State chooses to revise its SIP to apply the 0.5 lb VOC/lb solids RACT equivalent to all sources, this should be as an alternative in addition to, rather than as a replacement for, the RACT limitations recommended in the CTG and already incorporated into most SIP's.

The 0.5 lb VOC/lb solids limit includes all solvent added to the ink: solvent in purchased ink, solvent added to cut the ink to achieve desired press viscosity, and solvent added to ink on the press to maintain viscosity during the press run. Method 24 test procedures and procedures to account for thinning solvent as specified in "Procedures for Certifying Quantity of Volatile Organic Compounds by Paint, Ink, and Other Coatings", EPA 450/3-84-019, must govern in determining VOC compliance of an ink in an enforcement situation.

This limit applies to flexographic printing and packaging rotogravure printing presses. Publication rotogravure presses are not covered by this guidance.

cc: Regional Administrator, Regions I-X
Chief, Air Branch, Regions I-X
Ron Campbell
Gerald Emison
B. J. Steigerwald

X

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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Washington, DC 20460 Telephone: 202/382-2848

16. ABSTRACT

The calculation of volatile organic compound emissions from graphic arts operations to determine compliance is often a complicated task, sometimes creating confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. EPA guidance for submitting data on ink formulations and performing basic calculations is contained in the document entitled "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings," EPA 450/3-84-019, published in December 1984. On June 19, 1985, two pages, III-4 and III-9, were revised and issued.

"A Guideline for Graphic Arts Calculations" takes the above guidance process one step further. Example calculations are included for basic emission problems, compliance determinations, control strategy problems, and complex emission problems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Inks Compliance Calculations Pollution Control Rotogravure Printing Flexographic Printing	Graphic Arts Calculations	

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