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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: 29 JUN 1983

SUBJECT: Exclusion of Exempt Solvents  
From VOC Calculations

FROM: G. T. Helms, Chief  
Control Programs Operations Branch (MD-15)

TO: Chief, Air Branch, Regions I-X

It has been brought to my attention that there has been some misunderstanding by various parties concerning the proper method of excluding exempt solvents from VOC calculations.

This memorandum is to clarify that exempt solvents should be subtracted out from coatings just like water, with the ultimate value of interest being the mass of VOC per unit volume of coating less exempt solvent and water.

Attached is a memorandum dated February 26, 1981, from David Salman, Chemical Applications Section, Chemical Petroleum Branch, to James Berry, Chief, Chemical Applications Section, Chemical Petroleum Branch, Emission Standards and Engineering Division. This document includes a discussion and examples of calculations related to the VOC content of coatings with exempt solvents.

Should you have any questions, please contact the Technical Guidance Section (Brock Nicholson or Bill Polglase, FTS 629-5516).

Attachment

DOW CHEMICAL U.S.A.

BARSTOW BUILDING  
2020 DOW CENTER  
MIDLAND, MICHIGAN 48640

May 13, 1983

Mr. Tom Helms  
Chief of Control Programs, Operations Branch  
Mail Drop 15  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

CALCULATION OF VOC CONTENT OF GRAPHIC ARTS INKS CONTAINING  
COSOLVENT BLENDS WITH NON-VOC SOLVENTS

Dear Mr. Helms:

We are writing you in accordance with a recommendation by David Salman in the Chemicals & Petroleum Branch of the U.S. EPA. It is our hope that you can clarify differing interpretations on the calculation of VOC from graphic arts inks containing the non-VOC solvents 1,1,1-trichloroethane and methylene chloride.

As you are aware, the Federal EPA has exempted these two solvents from the definition of VOC. Federal Register references on that exemption are:

42 FR 35314 of July 8, 1977  
42 FR 3274 of January 16, 1979  
44 FR 32042 of June 4, 1979  
45 FR 32424 of May 16, 1980  
45 FR 48941 of July 22, 1980

To date, 92% of the States with SIP's on VOC's have exempted, 1,1,1-trichloroethane from the definition of VOC and from subsequent control of VOC in surface coatings and graphic arts. About 88% of these States have similarly exempted methylene chloride.

In the State of Tennessee, a graphic arts company, which has been working closely with its local EPA representative, is ready to use this option to meet VOC emission limitations. However, a question has arisen on how to treat the non-VOC solvent in determination of VOC content from their gravure inks. Specifically, one materials supplier believes that the way the regulations are written preclude 1,1,1-trichloroethane and methylene chloride being blended with VOC cosolvents. In their opinion, it is an "all or nothing" situation. The various States SIP's read:

"The volatile fraction of the ink, as applied to the substrate, contains 25.0 percent by volume or less of organic solvent and 75.0 percent by volume or more of water;"

Since 1,1,1-trichloroethane and methylene chloride are neither (volatile) organic compounds nor water, the supplier interprets the above to mean that any ink using a blend of 1,1,1-trichloroethane and/or methylene chloride with other organic solvents will always calculate to 100% organic solvent.

Mr. Tom Helms May 13, 1983 Page Two

This has not been the interpretation by other parties for graphic arts or other surface coatings. Interpretation by most State and Federal regulators has been that these solvents should be treated as water is treated in the calculation of VOC. (See the enclosed February 26, 1981, memo on "VOC Content of Coatings with Exempt Solvents" by David Salman.)

We would deeply appreciate whatever guidance you can provide us or the various regional offices of the EPA on the calculation of VOC content of graphic arts inks containing cosolvent blends with the non-VOC solvents. Please feel free to call us for specifics of particular customer usage.

Sincerely,

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Enclosures

cc: Mr. Eric Flowers  
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Mr. David Salman  
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U.S. Environmental Protection Agency  
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711

DATE: FEB 26 1981

SUBJECT: VOC Content of Coatings with Exempt Solvents

FROM: Dave Salman  
Chemical Applications Section, CPB (MD-13)

TO: James Berry, Chief  
Chemical Applications Section CPB (MD-13)

Many States have exempted certain volatile organic compounds of negligible photochemical reactivity, such as 1,1,1-trichloroethane and methylene chloride from their VOC rules. Recently I was asked by a representative of a major supplier of such solvents how to calculate the reactive (Footnote 1) VOC content of a coating that contained both VOC and exempt solvents (Footnote 2). I suggested that exempt solvents should be subtracted out from coatings just like water with the ultimate value of interest being the mass of VOC per unit volume of coating less exempt solvent and water (Footnote 3). I provided several sample calculations. These examples are attached.

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(Footnote 1) The word reactive has been dropped after this point. All subsequent references to VOC in this memo and attachments mean reactive VOC.

(Footnote 2) The term exempt solvent as used in this memo and attachments means those compounds of negligible photochemical reactivity that States are not required to control in their ozone SIPs. These compounds are listed in Attachment III.

(Footnote 3) Since coatings that contain exempt solvents such as 1,1,1-trichloroethane and methylene chloride are not likely to also contain water as a solvent, the less water term has been dropped from the attached examples.

ATTACHMENT I

Given the mass of VOC and mass of exempt solvent per unit volume of coating, determine the mass of VOC per unit volume of coating less exempt solvent.

Let  $x$  = mass of exempt solvent per unit volume of coating

$y$  = mass of VOC per unit volume of coating

$d$  = density of exempt solvent

$z$  = mass of VOC per unit volume of coating less exempt solvent

$$\text{Then } z = \frac{y}{1 - \frac{x}{d}}$$

Example 1 - Each gallon of coating contains 3 pounds of VOC and 2 pounds of exempt solvent. The density of the exempt solvent is 11 pounds per gallon.

$$z = \frac{3}{2} = 3.7 \text{ pounds of VOC per gallon of coating less exempt solvent}$$

$$1 - \frac{0.2}{11}$$

Example 2 - Each liter of coating contains 0.2 kg of VOC and 0.4kg of exempt solvent. The density of the exempt solvent is 1.3 kg per liter.

$$1 - \frac{0.2}{1.3} = 0.3 \text{ kg of VOC per liter of coating less exempt solvent}$$

Note: The term VOC as used above means reactive VOC only.

#### ATTACHMENT II

A paint formulator wants to add both VOC and exempt solvent to 0.25 gallons of coating solids to make 1 gallon of coating. The coating must meet an emission limit of 3 pounds of VOC per gallon less exempt solvent. What is the maximum amount of VOC that can be added? How much exempt solvent should be added to make 1 gallon of coating?

The answer to this problem depends on the density of the VOC and exempt solvent. If we assume that the VOC density is 7.2 pounds per gallon, the exempt solvent density is 11 pounds per gallon, and let:

x = maximum pounds of VOC that can be added

$$\text{Then: } \frac{x}{.25 + \frac{x}{7.2}} = 3$$

$$x = .75 + \frac{x}{2.4}$$

$$.58x = .75$$

$$x = 1.3 \text{ pounds VOC}$$

Since the VOC has density 7.2 pounds per gallon, this is equivalent to

$$\frac{1.3}{7.2} = .18 \text{ gallons VOC}$$

Finally, to make a full gallon of coating the formulator must still add:

$$1 - .25 - .18 = 1 - .43 = .57 \text{ gallon exempt solvent}$$

or

$$.57 \times 11 = 6.3 \text{ pounds exempt solvent}$$

If VOC or exempt solvent with different densities were used the results would differ. The same calculation can be done using the appropriate solvent densities.

Note: The term VOC as used above means reactive VOC only.

#### ATTACHMENT III

Compounds of negligible photochemical reactivity that States are not required to control in their ozone SIPs of February 1981:

methane  
ethane  
1,1,1-trichloroethane (methyl chloroform)  
trichlorotrifluoroethane  
methylene chloride  
trichlorofluoromethane  
dichlorodifluoromethane  
chlorodifluoromethane  
trifluoromethane  
dichlorotetrafluoroethane  
chloropentafluoroethane

Federal Register References:

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42FR35314 - July 8, 1977  
44FR32042 - June 4, 1979  
45FR32424 - May 16, 1980  
45FR48941 - July 22, 1980