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Category: 33 – Definition of VOC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Volatile Organic Compounds

FROM: James C. Berry, Chief
Chemical Application Section (MD/13)

DATE: August 16, 1978

TO: John Calcagni
Control Programs Operations Branch (MD/15)

We have been asked a number of times about the EPA definition of VOC. I am certain you too will be asked in future weeks. The attached memo by Vera Gallagher summarizes our rationals. If you have any questions, please call me.

Enclosure

cc: Don Goodwin
Jack Farmer
Bob Walsh
Dave Patrick
Jim Durham

Enclosure

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: July 1, 1978

SUBJECT: Definition of "Volatile Organic Compound"

FROM: Vera Gallagher
Chemical Application Section

TO: James C. Berry, Chief
Chemical Application Section

The Standards Development Branch has asked several times during the development of a draft preamble for the metal furniture industry, about the official definition of Volatile Organic Compounds (VOC) and the analytical method to be used for certifying the VOC content of a coating. Our section discussed these same issues many times during the development of the control techniques guidelines for surface coating and the standard support document for automobiles and light duty trucks. Although we have referred to VOC in many different reports, EPA has not yet selected a formal Agency "definition."

Much of this reticence stems from the lack of information about the entire phenomena of atmospheric chemistry. Certainly it would be in everyone's best interest that the definition of VOC result in regulation of only those organic compounds that participate in the formation of photochemical oxidants. (Since, there is no National Ambient Air Quality Standard for organic compounds, it would be wasteful if our regulations forced an increase in manufacturing costs to restrict emissions of an organic that does not participate in formation of oxidant). The information now available indicates that almost any organic compound (with five exceptions*) that remains air-borne in the vapor state will eventually form oxidant. With no other information on what will react, we are left with two major issues for which answers are critical before we can perfect the definition of VOC.

- 1) What compounds, when emitted in the gaseous state from the ovens, will not condense and precipitate but rather remain air-borne and ultimately react to form photochemical oxidant?
- 2) What is the fate of organic compounds emitted as an ultra-fine aerosol which remains air-borne for extended periods because of its extremely small particle size, but would not normally be expected to evaporate based on its relatively high vapor pressure? (Some printing operations emit tons of such matter annually). There is no evidence of precipitation of these compounds, it is very possible that they remain air-borne until they evaporate and then react to form oxidants.

- methyl chloroform
methane
ethane
trichlorotrifluoroethane
acetonitrile

These unanswered questions and a search for compromise have delayed our attempts to prepare an official EPA "definition" although the following is an excerpt from the new "Control Techniques for Volatile Organic Emissions from Stationary Sources.

"Organic compounds include all compounds of carbon except carbonates, metallic carbides, carbon monoxide, carbon dioxide, and carbonic acid. A volatile organic compound (VOC) is any organic compound that, when released to the atmosphere, can remain long enough to participate in photochemical reactions. While there is no clear line of demarcation between volatile and nonvolatile organics, the predominant fraction of the VOC burden are compounds which evaporate rapidly at ambient temperatures. Almost all organics which can be considered VOC have vapor pressures greater than 0.1 mm Hg at standard conditions (20 degrees Celsius, 760 mm Hg)."

None the less, the actual determination of how much VOC is in an exhaust stream will ultimately depend on a reference test method. In previous NSPS, the test method itself was the mechanism that defined the pollutant. For example, Method #5, as published in the Federal Register, defines "particulate" as anything entrapped by the filter in a sample train. In no case, that we are aware of, does EPA attempt a quantitative definition such as "particulate is a small round (or irregular) piece of solid, (or liquid)..". We can attempt to describe in narrative form what the reference test method is believed to identify, but it seems the test method itself must ultimately be the reference "definition".

VOC emissions differ from particulate, however, in that we often will know the quantity and composition of organic emissions that would be expected from a process; especially during the application and cure of some coatings. We can use the manufacturers' formulation and applicators' dilution to define, with reasonably good precision, the total mass of solvent that should be emitted. (For purposes of this discussion we will ignore the varied reaction possibilities within a high temperature cure process that may retain some organic solvent content through formation of condensation products that would normally have been emitted). We do not know, however, if the higher boiling organics that vaporize from the coating film within an oven should be of interest to us from a regulatory standpoint. There is no question about those compounds with high vapor pressures such as methyl ethyl ketone or hexane. The compounds with unknown fate are those with much lower vapor pressures such as the naphtha blends manufactured under various trademarks (for example, Texanol-R and Solvessos-R) and the family of acetate compounds, as shown in Attachment 1.

Attachment 1 also graphically displays two previous attempts to define the materials that are precursors to oxidant. The first was developed by Los Angeles County APCD as part of their Rule 66 which was formulated in the mid 1960's. It is based on materials with a vapor pressure greater than 0.5 mm of mercury at 110 degree Celsius. The more conservative definition used by ESED in the Guidelines for surface coating applications (vapor pressures greater than 0.1 mm at 20 degrees Celsius) is also shown. There probably are organic compounds that would not be identified as VOC by either definition that, under the proper emission conditions, would react photochemically. Obviously, the Los Angeles definition is broader and there would be many more photochemically reactive compounds that "escape" the ESED definition. Unfortunately, we are now unable to identify all of the compounds that actually contribute to photochemical smog; furthermore, even if we could, in some cases their participation could depend on the manner in which they are introduced into the environment. Consequently, any narrative definition is of informational value only unless we should choose to identify it as the "reference test method."

Since the present analytical data does not allow us to structure a perfect definition of VOC that may include or exclude questionable compounds based on their reactivity, the physical property we chose (0.1 mm at 20 degrees Celsius) can be expected to assist us in achieving major improvements in air quality without requiring control of a large number of organic materials that may not react to form oxidant. A laboratory technique for analyzing the solvent content of a coating is a more realistic "definition" of VOC. One was provided in Volume II" when we recommended that ASTM method D 2369-73 "Standard Method of Test for Volatile Content of Paint, Varnish, Lacquer, and Related Products" be used as the reference method to determine the VOC in air dry coatings.

It is unfortunate, however, that this ASTM Method may not be suitable for determining the total VOC content of all coatings. Many used by those industries for which EPA has published Guidelines or ESED has projected NSPS) are cured at elevated temperatures. The reference ASTM test does not simulate oven conditions to quantify the additional amount of VOC which may be emitted from oven-cured volatiles which have been reported to possibly amount to an additional 5 to 30 weight percent beyond that measured by the ASTM Method. Although we have no data yet, PPG Industries, a coating manufacturer, is studying this problem and will supply results of some of their tests once they are completed. Roger Shigehara will work with PPG to see if they obtain common results.

Both Dr. Wicks, Professor and Chairman, Polymer and Coatings Department, North Dakota State University and Roger Shigehara have suggested that the coating industry be invited to participate in the development of any new standard analytical method for determining the VOC content of oven-cured coatings. Within the Chemical Analysis Section, we have considered a "Standard" test method that would analyze each coating at the manufacturer's recommended cure temperature. Dr. Wicks feels this would be too cumbersome and urged selection of one temperature in the 240-260 degrees-F range to simplify the analytical problems. Both Dr. Wicks and Dr. Lou LeBras, Technical Director of PPG Industries have suggested that measurement of volatiles released as a result of cross linking may be so complex because of

the many factors involved in curing a coating, that we might be wiser to ignore them for now until the impact of our present efforts on ambient air quality can be determined. Then, if more control is required, a refinement of the regulations could include limits on "oven cure" VOC.

Because of the complexity of these problems and the strong possibility that these issues cannot be resolved until more scientific data is available on photochemically reactive compounds and the physical conditions under which they will react, we recommend use of the ASTM Test Method D2369-73 for determining compliance with the standards. If future data shows that more stringent control is required, new testing procedures can be developed to meet the need.

cc: Basil Dimitriades
Roger Shigahara
Gene Smith
Bob Walsh
George Walsh