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Category: 15 – Solvent Metal Degreasing

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

DATE: JUN 20, 1979

SUBJECT: Modifications to Recommendations for Solvent Metal Cleaning

FROM: Richard G. Rhoads, Director
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TO: Director, Air and Hazardous Materials Division, Regions I-X

In the Control Technique Guideline for Solvent Metal Cleaning, the operating requirements for open top vapor degreasers include the following specification for changes in the vapor level:

"The vapor level should not drop more than 10 cm (4 in) when the workload enters the vapor zone."

Recently the effectiveness and practicality of this specification has been questioned. The Emission Standards and Engineering Division of OAQPS has reviewed this issue and has concluded that this specification may not necessarily reduce emissions and will cause compliance problems for a significant number of sources. A summary of the analysis is attached.

Accordingly, State plans which do not include this provision for open top vapor degreasers should be recommended for approval. States with final adopted regulations that include this restriction should be advised of potential implementation problems with the provision. Where practical, States should be encouraged to amend their plans to delete this provision. In the interim, Regional Offices should take no steps to implement this provision.

Attachment

cc: Mr. Ed Reich, DSSE
Mr. Don Goodwin, ESED

(NOTE: The attachment is 42 FR 35314, July 8, 1977, "Air Quality; Clarification of Agency Policy Concerning Ozone SIP Revisions and Solvent Reactivities".)

ENVIRONMENTAL PROTECTION AGENCY

[FRL 729-5]

AIR QUALITY

Recommended Policy on Control of Volatile Organic Compounds

PURPOSE

The purpose of this notice is to recommend a policy for States to follow on the control of volatile organic compounds (VOC), which are a constituent in the formation of photochemical oxidants (smog). This notice does not place any requirements on States; State Implementation Plan (SIP) provisions which offer reasonable alternatives to this policy will be approvable. However, this policy will be followed by EPA whenever it is required to draft State Implementation Plans for the control of photochemical oxidants.

BACKGROUND

Photochemical oxidants result from sunlight acting on volatile organic compounds (VOC) and oxides of nitrogen. Some VOC, by their nature, start to form oxidant after only a short period of irradiation in the atmosphere. Other VOC may undergo irradiation for a longer period before they yield measurable oxidant.

In its guidance to States for the preparation, adoption, and submittal of State Implementation Plans published in 1971, the Environmental Protection Agency emphasized reduction of total organic compound emissions, rather than substitution. (See 40 CFR Part 51, Appendix B.) However, in Appendix B, EPA stated that substitution of one compound for another might be useful where it would result in a clearly evident decrease in reactivity and thus tend to reduce photochemical oxidant formation. Subsequently, many State Implementation Plans were promulgated with solvent substitution provisions similar to Rule 66 of the Los Angeles County Air Pollution Control District. These regulations allowed exemptions for many organic solvents which have now been shown to generate significant photochemical oxidant.

On January 29, 1976, EPA published its "Policy Statement on Use of the Concept of Photochemical Reactivity of Organic Compounds in State Implementation Plans for Oxidant Control." The notice of availability of this document appeared in the FEDERAL REGISTER on February 5, 1976 (41 FR 5350).

The 1976 policy statement emphasized that the reactivity concept was useful as an interim measure only, and would not be considered a reduction in organic emissions for purposes of estimating attainment of the ambient air quality standard for oxidants. The document also included the following statement:

> Although the substitution portions of Rule 66 and similar rules represent a workable and acceptable program at the present time, better substitution regulations can be developed, based on current knowledge of reactivity and industrial capability. EPA in collaboration with State and industry representatives will formulate in 1976 an improved rule for national use.

SUMMARY

Analysis of available data and information show that very few volatile organic compounds are of such low photochemical reactivity that they can be ignored in oxidant control programs. For this reason, EPA's recommended policy reiterates the need for positive reduction techniques (such as the reduction of volatile organic compounds in surface coatings, process changes, and the use of control equipment) rather than the substitution of compounds of low (slow) reactivity in the place of more highly (fast) reactive compounds. There are three reasons for this. First, many of the VOC that previously have been designated as having low reactivity are now known to be moderately or highly reactive in urban atmospheres. Second, even compounds that are presently known to have low reactivity can form appreciable amounts of oxidant under multiday stagnation conditions such as occur during summer in many areas. Third, some compounds of low or negligible reactivity may have other deleterious effects.

Of the small number of VOC which have only negligible photochemical reactivity, several (benzene, acetonitrile, chloroform, carbon tetrachloride, ethylene dichloride, ethylene dibromide, and methylene chloride) have been identified or implicated as being carcinogenic, mutagenic, or teratogenic. An additional compound, benzaldehyde, while producing no appreciable ozone, nevertheless, forms a strong eye irritant under irradiation. In view of these circumstances, it would be inappropriate for EPA to encourage or support increased utilization of these compounds. Therefore, they are not recommended for exclusion from control. Only the four compounds listed in Table 1 are recommended for exclusion from SIP regulations and, therefore, it is not necessary that they be inventoried or controlled. In determining reductions required to meet oxidant NAAQS, these VOC should not be included in the base line nor should reductions in their emission be credited toward achievement of the NAAQS.

It is recognized that the two halogenated compounds listed in Table 1 (methyl chloroform and Freon 113) may cause deterioration of the earth's ultraviolet radiation shield since they are nearly unreactive in the lower atmosphere and all contain appreciable fractions of chlorine. The Agency has reached conclusions on the effects of only the fully halogenated chlorofluoroalkanes. The Agency on May 13, 1977 (42 FR 24542), proposed rules under the Toxic Substances Control Act (TSCA) to prohibit the nonessential use of fully halogenated chlorofluoroalkanes as aerosol propellants. The restrictions were applied to all members of this class, including Freon 113, since they are potential substitutes for Freon 11, Freon 12, Freon 114, and Freon 115, which are currently used as aerosol propellants. The Agency is planning to investigate control systems and substitutes for nonpropellant uses under TSCA, as announced on May 13. Methyl chloroform is not a fully halogenated chlorofluoroalkane. Rather, it is among the chlorine-containing compounds for which the Agency has not completed its analysis; EPA has not yet concluded whether it is or is not a threat to the stratospheric ozone. Therefore, it has been placed on this list as an acceptable exempt compound. As new information becomes available on these compounds, EPA will reconsider the recommendation.

The volatile organic compounds listed in Table 2, while more photochemically reactive than those in Table 1, nevertheless do not contribute large quantities of oxidant under many atmospheric conditions.

TABLE 1.—*Volatile Organic Compounds of Negligible Photochemical Reactivity That Should Be Exempt From Regulation Under State Implementation Plans*

Methane
Ethane
1,1,1-Trichloroethane (Methyl Chloroform)[1]
Trichlorotrifluoroethane (Freon 113)[1]

[1] These compounds have been implicated as having deleterious effects on stratospheric ozone and, therefore, may be subject to future controls.

TABLE 2.—*Volatile Organic Compounds of Low Photochemical Reactivity*

Propane
Acetone
Methyl Ethyl Ketone
Methanol
Isopropanol
Methyl Benzoate
Tertiary Alkyl Alcohols
Methyl Acetate
Phenyl Acetate
Ethyl Amines
Acetylene
N,N-dimethyl formamide

Only during multiday stagnations do Table 2 VOC yield significant oxidants. Therefore, if resources are limited or if the sources are located in areas where prolonged atmospheric stagnations are uncommon, priority should be given to controlling more reactive VOC first and Table 2 organics later. Table 2 VOC are to be included in base line emission inventories and reductions in them will be credited toward achievement of the NAAQS. Reasonably available control technology should be applied to significant sources of Table 2 VOC where necessary to attain the NAAQS for oxidants. New sources of these compounds will also be subject to new source review requirements.

Perchloroethylene, the principal solvent employed in the dry cleaning industry, is also of low reactivity, comparable to VOC listed in Table 2. It was not included in Table 2 because of reported adverse health effects. Uses, environmental distribution, and effects of perchloroethylene currently are being studied intensively by occupational health author-
ethylene currently are being studied investigations may have major impact on

industrial users. In designing control regulations for perchloroethylene sources, particularly dry cleaners, consideration should be given to these findings as well as industry requirements and the cost of applying controls. Available control technology is highly cost effective for large perchloroethylene dry cleaning operations. However, for coin-operated and small dry cleaners, the same equipment would represent a heavy economic burden.

As part of its continuing program, EPA will review new information relative to the photochemical reactivity, toxicity, or effects on stratospheric ozone of volatile organic compounds. Where appropriate, additions or deletions will be made to the lists of VOC in Tabels 1 and 2.

DISCUSSION

Most air pollution control regulations applicable to stationary sources of VOC in the United States are patterned after Rule 66 of the Los Angeles County Air Pollution Control District (presently Regulation 442 of the Southern California Air Pollution Control District). Rule 66 and similar regulations incorporate two basic strategies to reduce ambient oxidant levels, i.e., positive VOC reduction and selective solvent substitution based on photochemical reactivity. Positive reduction schemes such as incineration, absorption, and the use of low-solvent coatings are acknowledged means of reducing ambient oxidant levels; they should be retained in future VOC control programs. In contrast, the utility of solvent substitution strategies has been questioned as more information on photo chemical reactivity has emerged.

EPA acknowledged the shortcomings of solvent substitution based on Rule 66 reactivity criteria in a 1976 policy statement (41 FR 5350). Findings were cited which indicated that almost all VOC eventually react in the atmosphere to form some oxidant. Concurrently, EPA initiated an investigation to consider implications of revising the solvent substituton aspects of Rule 66. Three separate forms were conducted with representatives of State and local air pollution control agencies, university professors, and industrial representatives with knowledge and expertise in the fields of atmospheric chemistry and industrial solvent applications. In addition, numerous discussions were held with acknowledged experts in the field. Topics of particular concern were:

Whether Rule 66 substitution criteria could be revised consistent with available reactivity data and yet be compatible with industrial processes and with product requirements.

Whether some compounds are of sufficiently low reactivity that they are not oxidant precursors and can be exempted from control under State Implementation Plans.

Whether the imposition of reactivity restrictions in addition to positive emission reductons will delay the development or implementation of promising technologies, particularly the use of water-borne and high-solids surface coatings.

Investigation showed that:

1. Solvent substitution based on Rule 66 has been directionally correct in the aggregate and probably effects some reductions in peak oxidant levels. However, because of the relatively high reactivity of most of the substituted solvents, the reduction is small compared to that which can be accomplished with positive reduction techniques. Revision of Rule 66 consistent with current knowledge of reactivity would eliminate the solvent substitution option for most sources in which substitution is new employed. Many of the organic solvents which have been categorized as having low photochemical reactivity are, in fact, moderately or highly reactive; they yield significant oxidant when subjected to irradiation in smog chambers designed to simulate the urban atmosphere.

2. A few VOC yield only negligible ozone when irradiated in smog chambers under both urban and rural conditions. Experiments conducted to date indicate that only methane and ethane, a group of halogenated paraffins, and three other organics—benzene, benzaldehyde, and acetonitrile—can be so classified. These compounds react very slowly yielding little ozone during the first few days following their release to the atmosphere. Available data suggest that none of the listed compounds contribute significant oxidant even during extended irradiation under multiday stagnation conditions.

The broad group "halogenated paraffins" includes important industrial solvents, most of which are chlorinated methanes and ethanes and chlorofluoroethanes. They find use as metal cleaning and dry cleaning solvents and as paint removers. Halogenated paraffins also serve as building blocks in the manufacture of other halogenated organics; these processes do not necessarily release significant VOC to the atmosphere.

3. Besides focusing on VOC of negligible reactivity, smog chamber studies show that a few additional VOC generate oxidant at a relatively slow rate. Under favorable atmospheric conditions, these VOC releases may not form oxidant until they have been transported substantial distances and become greatly diluted. However, under multiday stagnation conditions such as occur during summer in many areas of the middle and eastern United States, there is the potential for these organics to undergo appreciable conversion to oxidant. The more important VOC in this category are acetone, methyl ethyl ketone, parchloroethylene, methanol, isopropanol, and propane. All except propane are industrial solvents. The latter, a gas under normal conditions, is associated principally with crude oil and liquefied petroleum gas operations.

4. The vast number of volatile organic compounds—particularly nonhalogenated VOC—yield appreciable ozone when irradiated in the presence of oxides of nitrogen. While there are measurable variations in their rates of ozone formation, all are significantly more reactive than VOC listed in Table 2. Quickly reactive VOC include almost all aliphatic and aromatic solvents, alcohols, ketones, glycols, and ethers.

5. Low photochemical reactivity is not synonymous with low biological activity. Some of the negligible or slowly reactive compounds have adverse effects on human health. Benzene, acetonitrile, carbon tetrachloride, chloroform, perchloroethylene, ethylene dichloride, ethylene dibromide, and methylene chloride have been implicated as being carcinogens, teratogens, or mutagens. In addition, benzaldehyde, which produces no appreciable ozone, nevertheless forms a strong eye irritant under irradiation. While their use might reduce ambient oxidant levels, it would be unwise to encourage their uncontrolled release. Additional halogenated organics are being investigated for possible toxicity.

Most of the related health information available at this time concerns acute toxicity. Threshold limit values (TLV's) have been developed for many VOC. They are appropriate for the healthy, adult work force exposed eight hours a day, five days a week. Experts suggest that more stringent levels should be established for the general population. Hazards represented by chronic and subchronic exposure are much more difficult to quantify than acute toxicity. Adverse health effects of the VOC cited above are generally recognized although not completely quantified. Chlorinated solvents currently are under intensive study.

6. Some VOC are of such low photochemical reactivity that they persist in the atmosphere for several years, eventually migrating to the stratosphere where they are suspected of reacting and destroying ozone. Since stratospheric ozone is the principal absorber of ultraviolet (UV) light, the depletion could lead to an increase in UV penetration with a resultant worldwide increase in skin cancer. The only in-depth analysis of this potential problem has focused on the chlorofluoromethanes (CFM), Freon 11 and Freon 12, because of their known stability and widespread use in aerosol containers. A report of the National Academy of Sciences concerning environmental effects of CFM's concluded that:

> • • • seletcive regulation of CFM uses and releases is almost certain to be necessary at some time and to some extent of completeness.

In response to the report of the National Academy of Sciences and other studies, EPA on May 13, 1977 (42 FR 24542), proposed rules to prohibit nonessential useage of fully halogenated chlorofluoroalkanes as areosol propellants. The restrictions were applied to all members of this class including Freon 113 since they are potential substitutes for Freon 11, Freon 12, Freon 114, and Freon 115 which are currently used as aerosol propellants.

Other stable halogenated solvents which are released in volumes comparable to the chlorofluoroalkanes also are suspected of depleting the earth's UV shield. Of major concern is the wide-

spread substitution of methyl chloroform (1,1,1 trichloroethane) for the photochemically reactive degreasing solvent trichloroethylene. Such substitution under Rule 66 generation regulations has already influenced industrial degreasing operations to the extent that methyl chloroform production has surpassed that of trichloroethylene in the United States. Any regulation in the area will have a marked effect on the production and atmospheric emissions of both solvents. Endorsing methyl chloroform substitution would increase emissions, particularly in industrial States that have not, heretofore, implemented Rule 66. On the other hand, disallowing methyl chloroform as a substitute or banning it altogether would significantly increase emissions of trichloroethylene even if degreasers were controlled to the limits of available technology. Presently, technology is only able to reduce emissions by approximately 50 percent. In metropolitan areas which have already implemented Rule 66, a return to trichloroethylene would have an adverse effect on ambient oxidant levels. In addition to being highly reactive, trichloroethylene has been implicated as a carcinogen.

Alternatives to the above-cited choices would be (1) development and application of highly efficient degreaser control systems and (2) replacement with an intermediate solvent which is neither reactive nor detrimental to the upper atmosphere. Major revisions would be needed to degreaser designs to improve vapor capture above the current best level. Anticipated design changes could add materially to degreaser costs. No alternative solvent is clearly acceptable from the standpoints of photochemical oxidant and stratospheric ozone depletion. Neither methylene chloride nor trichlorotrifluoroethane are reactive, but, like methyl chloroform, are suspected of causing damage to the stratospheric ozone layer. In addition, methylene chloride is a suspect mutagen. Perchloroethylene, the principal dry cleaning solvent, does not present a hazard to the stratosphere but has been implicated as being a carcinogen and also reacts slowly in the atmosphere to form oxidant.

7. Organic solvents of low or negligible photochemical reactivity have only limited use in many industries. Most are chlorinated organics that find principal applications as cleaners for metals and fabrics. A few nonhalogenated VOC such as acetone, methyl ethyl ketone, and isopropanol are of low reactivity but these can't possibly satisfy all the myriad needs of the paint, plastics, pharmaceutical, or many other industries. While users of reactive VOC usually can employ effective control equipment to recover or destroy VOC emissions, they seldom have the option of applying reactivity considerations in choosing solvents. Applying reactivity restrictions to the surface coating industry would be especially disadvantageous since it would greatly inhibit the development of low-solvent coatings; essentially all of the organic solvents used to constitute high-solids coatings and water-borne coatings are, in fact, highly reactive.

8. It is recognized that smog chamber studies conducted to date are incomplete because many organic compounds have not been examined and it has been impossible to duplicate all atmospheric situations. For example, there has been only limited examination of oxidant formation under relatively high ratios of VOC to NO_x (30:1 and greater), comparable to rural conditions. Any policy on photochemical reactivity necessarily has to be open to revision as new information is developed which may show specific organic compounds to be more or less photochemically reactive than indicated by current data.

Dated: June 29, 1977.

EDWARD F. TUERK,
Acting Assistant Administrator for Air and Waste Management.

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