Air Pollution Regulation of Nonvehicular, Organic-Solvent Emissions by Los Angeles Rule 66¹

G. R. MAHER, E. I. du Pont de Nemours and Company Inc., Detroit, Michigan

Abstract

In an effort to further their control of sources emitting organic solvents into the atmosphere, the Air Pollution Control District of Los Angeles County, Calif., successfully secured passage of Rule 66 into law July 28, 1966. Rule 66 specifically relates to the control of organic solvent emissions from stationary sources. This paper directs itself to a discussion of the technical aspects used by the Air Pollution Control District in establishing which organic solvents contribute most significantly to the formation of photomechanical smog, eye irritation, and ozone. It also draws attention to the very specific topography of Los Angeles County. And it suggests that air pollution control authorities elsewhere be made cognizant of this in establishing controls on organic solvent emissions in their localities, so as not to be unnecessarily harsh and restrictive.

Introduction

It is generally known that Los Angeles began to experience smog in a serious way long before most other cities recognized that some day a smog problem might appear at home. Therefore it is quite natural that Los Angeles County has taken the lead in passing smog abatement recognitions

ment regulations.

The State of California legislature approved creation of the Air Pollution Control District of Los Angeles County on October 14, 1947. Almost immediately all outdoor burning was banned. Then the Air Pollution Control District moved against smoke emission from industrial and utility powerhouse stacks. It also placed stringent limits on the sulphur content of fuels. But over the years, even with these regulations, smog persisted.

So beginning with the 1966 model cars, exhaust-emission control devices were required by a State of California law. And now Rule 66 is the latest control enacted into law. It is directed at controlling nonvehicular emissions of organic solvents into the atmosphere in order to curtail further the formation of photochemical smog with its eye irritation, high ozone content, aerosol haze, and plant-damage effects. Thus there has been a continuing effort on the part of the Air Pollution Control District of the County of Los Angeles to seek out and control significant sources of air pollution.

This paper will review Rule 66 in an effort to highlight its purpose and to cover its control effect on industry and the general public. No effort is made to discuss the involved chemistry of probable photochemical reactions in the atmosphere.

Inventory

The Air Pollution Control District of Los Angeles County inventoried the organic solvents being emitted into the atmosphere in a 24-hour period in their county. They found that 550 tons were daily being emitted from nonvehicular sources. Whereas this tonnage is not great compared with the 1,930 tons of hydrocarbon solvent emissions each day from motor vehicles, it was still deemed desirable of control.

The major contributor to the 550-ton daily emission of organic solvents was industrial, commercial, and residential painting. However industry stacks were releasing 205 tons of the daily total into the atmosphere.

¹ Presented at the AOCS Short Course, East Lansing, Aug. 29-Sept. 1, 1966.

The individual organic solvents which comprised the 550 tons were considered by the Air Pollution Control District in establishing their smog chamber test program. This same smog chamber facility had previously been used in measuring the relative rate of photochemical reactivity of hydrocarbon organic solvents in motor vehicle fuels. And with this information and technique as background, organic solvents of the types found in the non-vehicular tonnage were tested in the smog chamber.

There are only a few smog chambers of approximately 1,100 cubic feet capacity but many of about 50-litre size. They are equipped with artificial sun lamps, instruments for recording formation of ozone, carbon monoxide, and nitrogen dioxide. Also they are provided with port openings for checking the eye irritation of an observer or a panelist.

Test organic solvents are added to the ambient air at the concentration of 4 ppm, which is in excess of that generally encountered, in order to hasten any photochemical reaction that may occur. In addition, nitric oxide is added at 2 ppm because of its regular presence in the atmosphere. The test atmosphere is irradiated for a total of six hours; eye irritation checks are made five minutes after the start of the test and at the end. Details for the operation of a smog chamber test may be found in the literature.

The Los Angeles test on organic solvents, based primarily on the extent to which eye irritation did or did not occur as well as on the photochemical formation of ozone or the lack of it, enabled the District to determine which solvents in their judgment should be controlled.

Controls

As a result they decided, in cooperation with industry representatives, that organic solvent-containing products are to be controlled as follows.

- 1. A maximum of 5% by volume of olefinic or cycloolefinic organic solvents may be present.
- 2. A maximum of 8% by volume of aromatic organic solvents having eight or more carbon atoms may be used.
- 3. Ketone organic solvents having a branched chain structure, such as methyl iso-butyl ketone, are limited to a maximum of 20% by volume.
- 4. A maximum of 20% by volume of toluene may be used.
- 5. Ethylbenzene, an aromatic organic solvent with eight carbon atoms, was given a special status and allowed a maximum of 20% by volume.
- 6. Trichloroethylene is restricted to a maximum of 20% by volume. This organic solvent did not respond as a significant eye irritant, nor did it produce ozone in objectionable amounts. Nevertheless the A.P.C.D. ruled that it should be controlled. However, additional tests are to be run in an effort to establish whether some change in its control should be made.

There is an indication that, by the control of the emission of these organic solvents, an 80% reduction in the photochemically reactive tonnage will be accomplished. And this, it is believed by the A.P.C.D., should be adequate while industry is still allowed the use of limited amounts of these solvents.

Exceptions

All other organic solvents therefore are not controlled by Rule 66 and, unless regulated by some other law, may be freely emitted into the atmosphere. Examples of such organic solvents are esters, ethers, alcohols, ketones (nonbranched), paraffins (normal, iso, and cyclo). These are uncontrolled only when they are free of the olefinic

type of unsaturation.

Inasmuch as commercial hexane is generally composed of paraffins (normal, iso, and cyclo) with perhaps a trace of benzene, Rule 66 will not require any control of emissions of this solvent into the atmosphere except under certain conditions: if the solvent vapors come into direct contact with flame; if the hexane vapors are emitted into the atmosphere in the presence of by-products of polymerization or other chemical change, such as occurs with baking or curing a paint film. In either of these events, it is necessary to incinerate the resulting effluent to CO₂ with 90% efficiency prior to emission into the atmosphere. This same requirement applies to any organic solvent if its vapors come in contact with flame or if its vapors are emitted into the atmosphere along with noxious by-products of polymerization or chemical reaction.

It is of possible interest to note that iso-paraffin and cyclo-paraffin solvents are considered borderline by the Los Angeles A.P.C.D. in photochemical reactivity. And, as a result, serious consideration was given to controlling their emission into the atmosphere. Fortunately, on the basis of additional smog chamber tests, they were left

uncontrolled in Rule 66.

Oil- and glycerine-containing products in which organic solvents are used, for example, paint, adhesives, coatings, etc., which are cured, baked, or polymerized in use in industry, must have such effluent incinerated to CO₂, with 85% reduction at 90% efficiency. This requirement of Rule 66 introduces the need for capital expenditures of some considerable amount for incineration facilities. The installed cost of incineration equipment for conversion of organic material to CO₂ at 90% efficiency is currently estimated at about \$10 per CFM. This cost, plus daily operating expenses, will probably lead to some consideration of compositions for paint, adhesives, coatings, etc., which will obviate the need for incineration.

This means that paints, adhesives, coatings, etc., which are film-forming by solvent evaporation without subsequent polymerization or chemical change, will be evaluated in-asmuch as they do not require incineration of the effluent when Rule 66-approved organic solvents have been used.

Cost

As usual, cost is of paramount importance, and many

Increased Market Competition Topic at ASA Convention

Increased competition for US soybeans in export markets combined with the nation's first billion-bushel soybean crop expected this fall will face the American Soybean Association's 47th annual convention at Peoria, Ill., Aug. 14-16, with some hard problems, says Chet Randolph, acting executive secretary-treasurer.

Many countries have increased production of fats and oils—most notable being Russia's record sunflowerseed crop last year—and have contributed to a world fats and oils surplus, according to Randolph. Russia and other East European countries have become net explorers of fats and oils instead of importers as they have been in the past.

Soybeans have long been the nation's No. 1 agricultural growth industry, Randolph says, but neither domestic nor foreign markets have shown the expected growth this year. As a result, the United States is faced with a carryover of over 100 million bushels this September. At the same time, farmers planted a record acreage to soybeans last spring and a billion-bushel crop is predicted.

These problems will be dealt with by convention speakers, says Randolph. The formal program will be held at Hotel Pere Marquette Aug. 14–15. There will be a field tour Aug. 16 to nearby farms and to see research work on soybean products in progress at the Northern Regional Research Laboratory in Peoria.

organic solvent-containing products which normally have low-cost aromatic petroleum solvents will be required by Rule 66 to replace some of the low-cost aromatic solvent with much higher priced esters, alcohols, etc. Naturally, ingenious formulating among competitors will tend to minimize the cost penalty introduced by Rule 66. However it would appear at this point that price increases of from 10-20% may be quite common, except where water-borne or odorless mineral spirits-based products are currently being used. And, in these cases, little or no price increase would be expected.

Where paint products are normally applied by spraying, a high CFM condition prevails to carry off the overspray. It has been found uneconomical either to adsorb on charcoal or incinerate the effluent. Therefore it is essential to use a paint product that complies with Rule 66 so that the effluent can be freely emitted, uncontrolled, into the atmosphere. But, as mentioned earlier, if the paint product requires baking, curing, or polymerization in a subsequent operation, such effluent, regardless of the organic solvents used, must be incinerated because of any noxious by-products such as aldehyde, acrolein, etc., which would otherwise be emitted into the atmosphere.

Where organic solvent-based products are used, there will be a point of decision based on the economics of either complying by using solvents which are allowed by Rule 66 or by incinerating the effluent. For example, where the product is spray-applied, it is generally uneconomical to incinerate the large volume of effluent from a spray booth so Rule 66-approved solvents would be used.

Other Cities

Other cities are currently seriously considering legislation aimed at abating air pollution by controlling the emission of photochemically reactive organic solvents into the atmosphere. San Francisco is expected to take action, possibly by the end of this year. Phoenix is studying its air pollution problem, as are other cities.

Certainly it is fervently hoped that, in those cities where some control seems to be necessary, the local topography, meteorology, and organic-solvent emissions form the basis for legislation rather than just a policy of mimicking Los Angeles' Rule 66. The conditions which prevail in Los Angeles are probably more severe than those found elsewhere, and it would be unnecessarily wasteful to legislate beyond what is required.

ASTM Committee E-19 on Gas Chromatography Plans October Meeting

The Sheraton-Palace Hotel in San Francisco, Calif., will be the setting for the 6th Annual Meeting of ASTM Committee E-19 on Gas Chromatography, to be held Oct. 9-11, 1967

The program will include discussions and formal presentations on 1) Quantitation of Gas Chromatography, with Chairmen Louis Mikkelsen, F & M Division, Hewlett-Packard; Frederick Baumann, Varian Aerograph; James Karohl, Perkin-Elmer; H. A. Hancock, Jr., E. I. duPont de Nemours and Company; 2) Other Forms of Chromatography, with Chairmen M. K. Brandt, Analtech, Inc.; J. C. Moore, Dow Chemical Co.; Sheldon Lambert, Shell Development Corporation; 3) Analysis of Food Flavors by Gas Chromatography, with Irwin Hornstein, USDA, Beltsville, Md.; and 4) Use of Derivative Techniques in Gas Chromatography, with J. C. Cavagnol, Chemagro Corporation.

Subcommittee meetings of E-19 will also be held to discuss progress in nomenclature and data standardization, research, methods standardization, standard materials, programs and papers.