

ILLINOIS POLLUTION CONTROL BOARD
September 29, 1975

IN THE MATTER OF)
PROPOSED AMENDMENTS TO) R75-3
CHAPTER 2: AIR POLLUTION)
REGULATIONS)
)

OPINION OF THE BOARD (by Mr. Dumelle):

This matter concerns proposed amendments to the definitions of photochemically reactive material and volatile organic material contained in Rule 201: Definitions of Chapter 2: Air Pollution Regulations of the Board's Rules and Regulations.

The amendments were proposed by Chairman Jacob D. Dumelle of the Pollution Control Board and, pursuant to Rule 204 of the Board's Procedural Rules, were set for hearing. The proposal, with an accompanying statement of need, was published on March 10, 1975 in Environmental Register #99 (Exhibit 1).

Public hearings on the proposed amendments, designated R75-3, were held on April 11, 1975 in Belleville and on April 18 and 29, 1975 at the Chicago Circle Campus of the University of Illinois. Much interest in the proposal was evidenced by the 350 people who attended the April 18 hearing alone. The record from these hearings consists of 18 exhibits and over 500 pages of testimony by witnesses from industry, city, state, and federal government, academia, and medicine. Public comments, numbering 142, were also received by the Board and are part of the official record.

The proposed amendments were intended to reduce the emissions of hydrocarbons to the atmosphere and thereby reduce the atmospheric levels of ozone (Exhibit 1). The emission reduction would occur as a result of more emissions being defined as being photochemically reactive and/or volatile organic, and thus subjected to the emission limitations of Rule 205 of the Air Pollution Regulations. In particular, the present rule defines photochemically reactive material in terms of concentrations of certain organics, with the result that many emissions contain compounds thought or known to participate in the formation of ozone and other oxidants, but are not, however, defined as being photochemically reactive and thus not regulated. The proposed definition of photochemically reactive material would include almost all organic emissions,

The Board expresses its appreciation to Mr. Edward H. Hohman, Assistant to the Board, for his work in this proceeding.

except for those specifically exempted, and would therefore regulate the compounds that form oxidants. Similarly, the proposed change in the definition of volatile organic materials, from 2.5 pounds per square inch absolute (psia) to 1.5 psia, would subject more emissions of organics to the limitations of Rule 205, and would therefore also tend to decrease the formation of oxidants according to Chairman Dumelle's proposal.

Our basic concern was with the excessive oxidant levels in Illinois. The air quality standard for photochemical oxidants measured as ozone, state and federal, is 160 micrograms per cubic meter (or 0.08 ppm) maximum 1-hour concentration not to be exceeded more than once per year. During July and August of 1974, several areas in Illinois exceeded this standard. According to the report "Oxidants in the Urban Atmosphere" (Exhibit 3), peak hour ozone levels equalled or exceeded 0.1 ppm on 24 occasions in Chicago, on 15 occasions in Joliet; and on 3 occasions in July in Cahokia, and on 4 occasions in July in Springfield. Since the air quality standard of 0.08 ppm can be exceeded only once a year, violations of the photochemical oxidant air quality standard occurred at each of these locations in Illinois. Furthermore, according to Exhibit 3, the levels of oxidants hadn't changed significantly during the period of 1964 to 1972 based on Continuous Air Monitoring Program (CAMP) data, and the oxidant levels had exceeded the air quality standard.

The relation between ozone and oxidants has recently come under scrutiny. It had been felt that ozone was the major constituent of photochemical oxidants; Exhibit 3 for example cites data that shows 70% of total oxidants to be ozone. Recent studies in California and Texas (part of Comment 111), however, show ozone levels significantly higher than oxidant levels, based on simultaneous measurements. In any case, the 1974 data does show ozone levels exceeding the standard. It therefore seems that there is and has been an oxidant/ozone problem in Illinois.

The importance of minimizing oxidants and ozone is based on their adverse effects on health and welfare. Exhibit 16, "Air Quality Criteria for Photochemical Oxidants", is the federal criteria document that summarizes the effects on human health, vegetation, and materials. Based on this document the air quality standard of 0.08 ppm was established. Comment 100, "Health Effects and Recommended Alert and Warning Systems for Ozone", prepared by the Environmental Health Resource Center, contains recent information regarding the effects of ozone on the pulmonary system, nervous system, and others. Finally, Dr. Gross of the University of Chicago testified that while the irritating effects of pollen may be worse than that of ozone, there is permanent damage to the respiratory system with ozone but not with ragweed pollen (R. 455-457).

Our proposal would, we believe, decrease the ozone levels by decreasing the emissions of certain precursor compounds that undergo atmospheric reactions to form ozone. Basically, photochemical oxidants are formed by the reactions between nitrogen oxides and certain organic compounds in the presence of sunlight. The exact details of all the atmospheric reactions are not known, but the important features are the following (Exhibit 3, pp. 35 to 46):

a) the photolysis of nitrogen dioxide (NO₂) in the presence of sunlight,



b) the formation of ozone (O₃) utilizing the free oxygen liberated in the previous reaction,



c) the destruction of ozone by the nitric oxide (NO) emitted to the atmosphere,



d) reactions competing with c) between organics, O₃, O, and nitrogen oxides to form photochemical oxidants including

1. Ozone,
2. Nitrogen dioxide and nitrogen containing products such as peroxyacetyl nitrate (PAN), and nitric acid, and
3. Partially oxygenated organics such as acrolein.

The organics that participate in the above atmospheric reactions are characterized as being photochemically reactive. Smog chamber studies, performed to identify the reactive organics, consist of irradiating a mixture of organics and nitrogen oxides with artificial sunlight for a certain period of time and measuring the oxidants produced. The record contains the smog chamber studies performed by Batelle-Columbus Labs (Exhibit 8), National Air Pollution Control Administration (Exhibit 13), Bureau of Mines (Exhibit 13), Shell Development Company (Exhibit 13), Los Angeles Air Pollution Control District (Exhibit 13), and Stanford Research Institute (Comment 89). A summary of the data into reactivity classes has been performed by the U.S. Environmental Protection Agency (U.S. EPA) (See pages 13 to 22 of Exhibit 5 "Proceedings of the Solvent Reactivity Conference"). While there were inconsistencies in the data from test to test, the U. S. EPA felt that 5 classes of reactivity were justified, with Class I containing compounds considered to be non-reactive (See

Table 5 of Exhibit 5). These Class I non-reactive compounds are contained in the proposed definition of photochemically reactive material as exemptions. Since they do not form significant quantities of oxidants, they do not have to be controlled, unless they create problems because of their odor or toxicity. There is apparently little atmospheric data showing the reactions that form oxidants, so it is necessary to rely on smog chamber studies, which for the most part are based on 6-hour irradiation times. The U.S. EPA points out, however, in Exhibit 5, that during long distance transport and extended irradiation times, even low reactivity organics may form appreciable quantities of oxidants. It may be necessary, therefore, to control the emissions of all organics except the non-reactive ones.

A recent document received by the Board, of which we hereby take official notice, is a draft document dated August 13, 1975 and published by the U.S. EPA entitled "Guidelines on Use of Reactivity Criteria in Control of Organic Emissions for Reduction of Atmospheric Oxidants". It classifies organics into 3 photochemical reactivity classes categorized as follows:

Class I (low reactivity) - Emissions need not be controlled, unless exposed to temperatures exceeding 175°F.

Class II (moderate reactivity) - Control is necessary. Oxidants are formed gradually and will contribute to atmospheric levels both at the point of release as well as at downwind locations, rural and urban.

Class III (high reactivity) - Control is necessary. Oxidants are formed rapidly in the vicinity of their release, and are major contributors within urban source areas.

The Class I compounds listed in this document contain the exemptions listed in our proposal plus several more not previously classified. The draft guideline states that the emission of any Class II or III compound must be considered an interim measure, and that the long range solution to an oxidant problem must be either the reduction of emissions or the substitution of Class I compounds.

Our proposed amendment to the definition of photochemically reactive materials is consistent with these goals, and were it not for other considerations to be described below, including the incompleteness of the record, we would be inclined to adopt the amendment as modified to include the following additional exemptions: partially halogenated paraffins (see discussion by Dow Chemical in Comment 89), acetic acid, aromatic amines, and hydroxyl amines.

As stated previously, the precursors, nitrogen oxides and reactive organics, form oxidants in the atmosphere. Thus to reduce oxidant levels, one should presumably reduce the emissions of reactive organics, nitrogen oxides, or both. The testimony

of Professor Quon was that reducing hydrocarbons alone would result in lower concentrations of ozone than reducing both hydrocarbons and nitrogen oxides simultaneously, based on the present atmospheric concentrations of these two pollutants at the Chicago CAMP station (R. 45).

The degree of reduction in emissions required to achieve compliance with the oxidant air quality standard is not known, although it is estimated to be large - in excess of 50% (R. 37). Dr. Quon believed that the proposed amendment would reduce the atmospheric levels of oxidants, including a "significant" reduction in the peak levels (R. 65-66). However, it is not known whether the proposed amendment would result in attainment of the air quality standard. Dr. Quon was of the opinion that it wouldn't and that amendments to reduce the emissions allowed by our Rule 205 (of the Air Regulations) were also necessary (R. 73-74).

Regarding the relationship between emission reduction and changes in ambient levels of oxidants, much was made of a Texas report that purportedly showed no decline in the frequency of high ozone levels even though hydrocarbon emissions were reduced by 80% in some areas (R. 239). Our review shows this document (Comment 114) does not contain sufficient data to confirm this statement, in that only the highest ozone values are given.

Testimony also concerned the high "natural" levels of ozone; levels that on occasion exceed the standards. Papers from New York State, Indianapolis, and Texas, submitted by DuPont as part of Exhibit 9, show ozone levels in rural areas and in air masses entering urban areas exceeding 0.08 ppm on occasion. Although one could argue that this was due to rural emissions of the precursor compounds reacting to form high levels of ozone, this is not necessarily the primary mechanism. The oft cited paper by Coffey and Stasiuk (Environmental Science and Technology Vol. 9, p. 59) contained in this record as part of Comment 41, indicates a belief that no significant ozone production occurs at their rural sites; the cause of high rural ozone levels say Coffey and Stasiuk, in another paper included as part of Exhibit 9, is long distance transport from emission sources and "a net generation of ozone in urban plumes at some distances downwind of the source area". Other papers contained in Exhibit 9 also show the regional characteristics of ozone, and indicated transport into rural areas. The truly "natural" ozone, that due to stratospheric leakage and naturally emitted organics, is in the range of 0.01 ppm to 0.07 ppm (Exhibit 2, enclosure to Comment 41). This ozone, upon entering urban areas, is scavenged by nitrogen

oxides and aerosols so that the net "natural" ozone input in urban areas is nearly zero; and an urban ozone problem is therefore caused primarily by the net formation of ozone from emitted precursors. Thus while many argued at the hearings that the ozone problem is due to "natural" inputs, the problem seems to be one of emissions of precursors from one geographic area contributing to ozone problems in a distant area.

We do not know, numerically, the impact the amendments would have in reducing emissions of photochemically reactive materials. The problem seems to be with the emission inventory. The Agency suggested that an updated, comprehensive hydrocarbon emission inventory is necessary (R. 338), which would presumably include information relating to reactive and non-reactive organics. The Agency attempted to estimate the reduction in Cook County (Exhibit 6). A discussion of this exhibit revealed the estimations and approximations used, and the incompleteness of the inventory (R. 311-337). Nevertheless it is a useful indicator of the emission reductions that could result from the adoption of the proposal. The estimated reduction is 6.5% of the total organic emissions in Cook County, including automobiles, or 13% of the non-automotive emissions (R. 322-323). This represents, according to Exhibit 6, a decrease in yearly emissions of organics of 26,340 tons. Similar estimates were not prepared for other areas of the state. While we do not know whether a reduction by 6.5% of the organic emissions in Cook County will solve the ozone problem, the U.S. EPA witness called the proposal "a step in the right direction...that should be incorporated into the overall oxidant strategy" (R. 357). His calculations were that a 68% to 70% reduction would be required (R. 367).

We turn now to a consideration of the proposed amendments themselves. As pointed out in Chairman Dumelle's proposal (Exhibit 1), not all emissions of reactive organics are included in the existing definition of photochemically reactive material. For example, an emission could contain 19.99% toluene, a known reactive organic, and not be defined as being photochemically reactive. As pointed out by Professor Quon, it is the mass emission rate that is important rather than the percentage (concentration in the effluent) (R. 104). The proposed amendment defines photochemically reactive material in terms of participating in atmospheric reactions to form oxidants. However, the definition is probably too inclusive because nearly every organic might react with "excited oxygen" (atomic oxygen) (R. 101). A revision of the proposed definition would then be warranted. The exemptions to the definition were criticized as being unusable in industrial processes for various reasons, including toxicity, gaseous phase, and odor. The properties of the exempted compounds and classes of

compounds are discussed in several portions of the record (R. 131-133, 153, Comment 9, Comment 22). In only two cases, that of Dow Chemical's recommendation regarding chlorinated paraffins and the printing industry recommendation of isopropyl alcohol, were suggestions made regarding either additions to the exemption list or changes to the proposed definition; other witnesses supported the existing definition of photochemically reactive material. It was pointed out by some that our existing regulation is being used in Los Angeles and is reducing ozone levels out there; but that may be due to Los Angeles levels being much higher (R. 85-88). Finally, although witnesses seemed to be under the impression that the proposal to amend the definition of photochemically reactive material would forbid the use of certain chemicals, we indicated at the hearings that our concern was with the emissions complying with the standard (R. 108).

The proposed amendment to the definition of volatile organic material is also intended to be more inclusive. It is consistent with the federal new source standard, and if nearly all organics are photochemically reactive, will decrease vapor emissions from storage and loading that could form oxidants (R. 34-35). The Agency supplied a list of chemicals that would be defined as volatile using the amendment (Exhibit 7). Some of them, for example methanol and benzene, have been exempted as being non-photochemically reactive, so there may be some inconsistency between the amendments to the two definitions. The emissions from bulk storage and handling facilities are estimated to represent 0.2% of the total organic emissions in the Chicago area (R. 492).

The economic impact of the proposed amendments could not be determined due to the incompleteness of the record. We were not successful in obtaining industry-wide statistics that would allow us to make the determination. The following discussion is, therefore, a qualitative discussion of the impact of the proposal.

The industries that would be affected by the proposed amendment include the following: paints and coatings manufacturing, painting and coating, asphalt manufacturing, asphalt roofing, printing, bulk storage, tire manufacturing, dry cleaning and degreasing. For those not in compliance with Rule 205: Organic Material Emission Standards and Limitations if the amendments were adopted, two compliance techniques are available: emission reduction, and reformulation or process modification. Examples of the former include incineration and carbon adsorption; and examples of the latter include water based paints and high solids coatings.

In order to reduce emissions of organics from stationary sources, one must collect the emissions from the source so that they

can be treated. Testimony was that in many cases there are multiple emission sources at a facility, for example paint spray booths or tire making machines, so that the collection equipment would consist of multiple hoods manifolded together; a system that may not be practical or feasible (R. 409). In addition, the testimony was that the volumes of exhaust air required to purge the organic emissions from the equipment may be large, which means that the concentrations of organics in the exhaust would be low (R. 135-136).

The two emission reduction techniques, incineration and carbon adsorption, have been and are being used to control certain emissions. Incineration is not applicable in all cases due to the unavailability of natural gas and the low concentration of organics in the exhaust that is incinerated (R. 136-137). Carbon adsorption has not been tried in all cases, although the solvent recovery feature seems attractive. In Chicago, there are two printing companies that practice solvent recovery, the first company uses a single solvent and is able to recover 85% of it for reuse, the second company is able to recover usable solvents unless the process is using a mixed solvent (R. 395-396). These companies are saving money as a result of the recovery systems (R. 188). As pointed out by one witness, the vapor recovery and reuse aspect of carbon adsorption is not applicable to mixtures of solvents; the same witness stated, however, that the solvents recovered could be and have been used as supplementary fuel (R. 270, 274).

Reformulation, in this proceeding, means modifying a process or product so as to reduce the amounts of certain organic compounds being used and emitted to the atmosphere; two possibilities being water based products and high solids products. Most of the testimony concerning reformulation involved paints and coatings, although there was testimony concerning degreasing agents. The coatings and paints used currently are formulated so that the volatile portion, the solvent, is by the present definition not photochemically reactive. Because of the various properties of the solvents currently used, and the properties of the proposed exemptions, it is impossible to reformulate all the paints and coatings using only the exemptions listed. Thus if one wanted to comply with the regulations as amended by the proposal, and the compliance technique selected was reformulation, water based or high solids coatings would be used.

Water based coatings have been in use for several years, for example Lucite house paint and emulsion type roofing materials (R. 226). It has been estimated that by 1978 to 1980, water based coatings will have replaced 30% of the solvent based variety (R. 170). However, the use of water based coatings in

industrial situations is hampered by the drying rate, which depends on temperature and humidity, and the resulting necessity to air condition the facility where the coatings are applied (R. 246-247). Water based roofing materials are expensive and are not suitable below 50°F (Comment 23).

High solids coating would be desirable because much less solvent would be used. Exhibit 17 shows the reduction in solvents usage by converting to high solids coatings. The Ford Motor witness described a program wherein Pintos were sold with powdered coatings that had been applied electrostatically (R. 294-295). The coating showed good survivability, and the main problem with the use of this coating technique seems to be the manufacturing application.

Many witnesses suggested that our existing Rule 205(f)(2)(D) be modified to increase the allowable organic content contained in the exception from 20% to 30%. We should do this, they say, to encourage the use of low solvent coatings (R. 139). Neither the decrease in development time nor the additional numbers of coatings that could be reformulated was known (R. 212-215). However, one witness testified that while only 2 of 35 industrial customers in Illinois can use coatings having organic contents of 20% or less, another 8 customers could use organic coatings having organic contents of 30% or less (R. 502-503). We believe Rule 205(f)(2)(D) to be an important alternative to the use of high solvent coatings, and we will therefore extend the deadline for the utilization of this coating method by two years in order to allow addition time for technology to develop.

We find the record in this proceeding to be inadequate for supporting the proposed definition changes. The main deficiencies are the impact of the amendment in reducing the emissions of reactive organics, and the effect of reducing precursor emissions in reducing atmospheric levels of oxidants. We will therefore dismiss the proceeding and request the Illinois Institute for Environmental Quality and the Illinois Environmental Protection Agency to undertake studies to cure the above deficiencies. The record in this proceeding will be available to the public for future proposed amendments.

This Opinion constitutes the Board's findings of fact and conclusions of law.

I, Christan L. Moffett, Clerk of the Illinois Pollution Control Board, hereby certify the above Opinion was adopted on the 29th day of September, 1975 by a vote of 4-0.


Christan L. Moffett, Clerk
Illinois Pollution Control Board