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A Review of the Air Pollution Research Program of the Smoke and Fumes Committee of the American Petroleum Institute†

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The cooperative efforts of the oil industry during World War I led to the organization, in 1919, of the American Petroleum Institute. The problem of pollution was recognized almost immediately, and early efforts on pollution control were directed to the problems of pollution of navigable waters. The Division of Refining of the Institute was organized in 1930 and included a Committee on Disposal of Refinery Wastes. This committee recognized that air pollution would eventually become a major problem for the petroleum industry, but at that time few refineries were located in areas where pollution of the air was of great enough concern to require corrective measures.

Following World War II and the enormous growth in population and industry on the West Coast, public pressure to halt the *smog* that plagued Los Angeles mounted rapidly. The California legislature enacted a law authorizing the formation of county air pollution control districts. The oil industry was subject to mounting criticism as being the chief contributor to air pollution in the Los Angeles area. Various regulations were passed governing the emission of atmospheric pollutants, but none of these proved effective in eliminating the nuisance. Within the Western Oil and Gas Association, an organization was formed to investigate the nature and origin of air pollution in Southern California. This organization, still active, has contributed considerably to the basic knowledge of the air pollution problem in Los Angeles through sponsored research.

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Formation of the Smoke and Fumes Committee

By 1951 it became apparent that the oil industry would continue to be blamed for the bulk of the air pollution, and it was also realized that the problem is not peculiar to the Los Angeles area but is of national importance. Although Los Angeles continues to get more than its share of the publicity, the same undesirable effects can and do occur in other parts of the country and the problem is of concern to the entire petroleum industry. At a meeting of the Division of Refining in November 1951, the Smoke and Fumes Committee was organized to set up a program to determine factually the causes and methods for control of objectionable atmospheric pollution resulting from the production, transportation, manufacture, and use of petroleum and its products. It was recognized that proper decisions with regard to the control of atmospheric pollutants could not be made without accurate, scientific information. It was also felt that, should legislation be regarded as necessary in some instances, fundamental knowledge based on reliable research rather than on theory or hypothesis should be available to government organizations to avert restrictive and uneconomic rulings of the type that had proved unnecessary in the past.

To carry out this program, research projects were established at qualified research centers where investigations were designed to determine the mechanisms leading to air pollution. A qualified scientist was selected from the oil industry to serve as a full-time Executive Secretary to administer the program. A group selected from top level research people was organized as a Technical Advisory Committee to guide the research program. Each research project was provided with a Project Advisory Committee composed of highly qualified industry scientists. These Project Advisory Committees maintain close contact with the research workers to offer suggestions to guide the project and to insure that results of the work are made available as promptly as possible.

The Smoke and Fumes Committee organization also includes a Publications Committee. Information resulting from research activities sponsored by the Smoke and Fumes Committee is distributed to other committees of

the API; to interested organizations in industry, research, and government; and to the public. Through the efforts of the Publications Committee, the dissemination of information has a prominent place in the Smoke and Fumes Committee program.

The Research Program

The Smoke and Fumes Committee has just completed its fifth year of sponsored research. The first project was established at the Stanford Research Institute on May 1, 1953. Research at SRI demonstrated that hydrocarbons and organic matter in the air react with oxides of nitrogen in sunlight to produce *smog* type air pollution characterized by its oxidizing ability. In connection with this work, methods were developed for the analysis of compounds suspected to be important in ozone-forming reactions. Included were methods to determine nitric oxide, nitrogen dioxide, aldehydes, ketones, and olefins present in the atmosphere. An infrared analyzer for hydrocarbons was completed and used to monitor hydrocarbon levels. The SRI project was completed in 1955, but sponsored research in air chemistry has been continued at the Franklin Institute using facilities which permit a more detailed study of atmospheric reactions.

The research at the Franklin Institute to determine the nature of chemical reactions in the air leading to air pollution is one of the most outstanding projects in the Smoke and Fumes Committee research program. The project was originally established to study reactions occurring in sunlight of oxides of nitrogen, ozone, and nitric acid vapor with hydrocarbons of the types present in gasoline. The objective was to determine the nature and relative amounts of the products formed. In order to work at the low concentrations occurring in the atmosphere, new analytical methods were required. Under Smoke and Fumes Committee sponsorship, the long-path infrared spectrometer (popularly known as "Silent Sam, the Smog Detective") was designed and built in Philadelphia, and the long-path infrared analytical techniques were developed. The device is a combination of a reaction vessel in which controlled amounts of pollutants in air can be irradiated by artificial sunlight and a highly sensitive measuring device by which the products of the reaction can be individually identified during the course of the reaction. Actually two of these devices are in use by the Franklin Institute — one at the laboratories in Philadelphia where their studies are concerned primarily with synthetic mixtures, and one in a mobile laboratory presently located in Pasadena, California, where both naturally occurring polluted atmospheres and synthetic mixtures are examined.

Researchers at the Franklin Institute have been able to show the relative influence of paraffins and olefins in the rate of smog-forming reactions. They have demonstrated the effect of varying concentration of nitrogen oxides in the reaction rates and on the products formed. They have discovered a new compound, or class of compounds, originally identified as "Compound X", which is formed as a result of reactions of hydrocarbons and oxides of nitrogen. Compound X has recently been further identified as peroxyacyl nitrite.

Work is in progress to synthesize and purify peroxyacyl nitrite to permit detailed study of the compound and its reaction products. Preliminary attempts to synthesize the compound from peracetic acid and silver nitrate and to purify it by gas chromatography have resulted in decomposition of the product in the purification step.

Future plans for the Franklin Institute project include studies of air chemistry in other areas of the Los Angeles Basin as well as continued research on synthetic mixtures to determine more of the nature of reactions leading to air pollution.

At the University of California at Riverside, the Smoke and Fumes Committee is supporting research on the effect of organic materials in the atmosphere on vegetation. Oxidant-type damage to plants is unique and is believed to be caused by oxidized organic materials. Although the damaging substance has not yet been identified, certain hydroxy hydroperoxides may be involved. Typical oxidant damage is produced with a mixture of ozone and certain olefins in air. The University of California at Riverside is conducting an extensive study of the products of the reactions of ozone and unsaturated hydrocarbons in an attempt to identify the products responsible for the damage.

As a part of this program, a plant exposure box was built in conjunction with the Franklin Institute long-path infrared cell at Pasadena and arranged so that the fumigants could be circulated through the cell and the box continuously using the long-path infrared cell to study the course of the reaction while exposing the plants. Reaction time and concentration of the fumigants have been found to be as important, or possibly more important, than olefin structure in determining formation of the phytotoxicant from ozone-olefin reactions.

In the realm of atmospheric pollutants other than hydrocarbons and oxides of nitrogen, sulfur compounds are probably the most frequently mentioned. Sulfuric acid aerosol has been suggested as one of the causes of reduced visibility accompanying air pollution. The Smoke and Fumes Committee sponsored a research project at the University of Illinois to study the rate of photochemical oxidation of sulfur dioxide in air. Results of this study proved that the gas phase oxidation of sulfur dioxide in naturally polluted atmospheres in natural sunlight is not significant in effectively reducing visibility. One hundred hours of intense noonday sunlight would be required to produce sufficient sulfuric acid aerosol to reduce the visibility in the Los Angeles atmosphere to one mile.

Liquid phase oxidation of sulfur dioxide in fog droplets nucleated with metallic salts has also been studied in the laboratory, but the conditions required to oxidize SO_2 to SO_3 in fog droplets are so specialized as to make the occurrence of this reaction highly improbable in naturally polluted atmospheres.

The ever increasing use of petroleum products and the concern over air pollution from burning hydrocarbons has given rise to many questions concerning the nature and extent of the contribution to air pollution from industrial and domestic burning devices. A project was placed at the Armour Research Foundation in 1953 to determine the quantity of hydrocarbon pollutants emitted to the atmosphere by furnaces burning petroleum products. A gas burner and an oil burner, considered typical of domestic units, were operated in a laboratory. Analysis of the gaseous effluents established that under even the most severe conditions of maladjustment, hydrocarbons were not present in gross amounts, and in normal burning conditions the flue gases from both oil and gas burners

contained no detectable quantities of hydrocarbon. To verify the laboratory results, a field survey of 74 installations, including both domestic and industrial burners, was conducted. Only eight installations showed hydrocarbons present in flue gas — all in amounts less than 100 ppm. From these results it must be concluded that industrial furnaces using heavy fuel oil and domestic units using furnace oil or gas do not release significant amounts of hydrocarbon contaminants to the atmosphere.

In the field of atmospheric analysis, the Smoke and Fumes Committee has also made, or is making, significant contributions. At the Kettering Laboratory of the University of Cincinnati, a project was established to conduct air analyses of a number of United States cities to determine the oxidant concentration during periods of air pollution for comparison with Los Angeles atmosphere. No abnormal ozone or oxidant contents, as noted in Los Angeles during *smog* attacks, were found in other cities, but in many instances the sulfur dioxide content of the air was much higher in other cities than in Los Angeles, indicating again that sulfur dioxide does not cause the visibility reduction associated with polluted air.

At the Truesdail Laboratories in Los Angeles, a recently placed project concerns the collection and analysis of gaseous carbon compounds in the atmosphere to determine the amount of carbon of fossil origin by analysis of carbon 14 in relation to the total carbon present. Samples of the atmosphere have been collected during periods of extreme air pollution and during periods of little or no pollution. The gaseous carbon fractions have been *fixed* as barium carbonate, and radiocarbon assay of the carbonate fractions is in progress in another laboratory. No results are available from this survey as yet, but the project is mentioned here to illustrate the type of work in which the Smoke and Fumes Committee is participating in an effort to provide a better understanding of air pollution problems.

Some of the sampling studies sponsored by the Smoke and Fumes Committee have pointed out that the micrometeorology of a sampling area can be extremely important in planning and conducting an air sampling program. The most recent research contract of the Smoke and Fumes Committee was awarded to the North American Weather Consultants at Santa Barbara, California, to study meteorological effects on atmospheric sampling. The project is designed to provide a handbook to assist engineers in the field in the planning, conducting, and interpreting results from gas tracer tests. The project is essentially a literature search based on recent experimental work with tracers and supplemented by the best available theory wherever necessary. North American Weather Consultants have assigned a research staff to the project, and it is expected the project will be completed this year.

New Tools for Research

In the development of new tools for air pollution research, the accomplishments of the Smoke and Fumes Committee are worthy of note. In addition to the long-path infrared cell and the associated techniques already described, the researches sponsored by the committee have produced: (1) A successful technique for tracing air pollution from a single source; (2) Gas chromatographic methods of analysis for the determination of the composition of exhaust gas; and (3) A method of detection of ozone suitable for use in continuous, portable instruments.

It is often desirable in the course of air pollution work to characterize quantitatively the pollution potential from a particular source. In a project sponsored at the Industrial Hygiene Foundation, a method was developed wherein the tracer substance, a small quantity of finely divided antimony oxide, is dispersed in a stack gas stream automatically for a desired period of time. Automatic sampling instruments, disposed at significant locations in the surrounding territory, are operated to collect the tracer material from the atmosphere. Analysis for the determination of the quantity of tracer in each sample involves neutron activation of the sample in a nuclear reactor and subsequent measurement of the induced radioactivity. This method provides the same high sensitivity normally associated with the use of a radioactive substance as a tracer, but avoids the hazards since the samples are made radioactive after the tests have been completed.

This tracer technique was successfully developed to determine the path of a gas from a given source. However, problems of the micrometeorology of the sampling area encountered in this project led to the placement of the North American Weather Consultants' project referred to earlier which will provide assistance in planning and interpreting these tests.

Through the Coordinating Research Council, the Smoke and Fumes Committee is contributing to the support of a project at the Bureau of Mines in Bartlesville, Oklahoma, on the development and application of gas chromatographic methods of analysis for the determination of the composition of exhaust gases. To date, the Bureau of Mines has developed equipment and techniques suitable for separation of the major portion of the hydrocarbon component of exhaust gas condensate into separate fractions with identification and quantitative measurement of each fraction. The technique developed to date is limited to C_9-and-lighter paraffins and C_8-and-lighter aromatics, olefins, and naphthenes, although some uncertainties exist in the identification of paraffins, naphthenes, and olefins above the C_6 molecular weight range. At present, methane is not collected by the sampling technique, but development of a method of analysis for methane by gas chromatography is in progress. In this project studies are currently under way to extend the analytical techniques to higher molecular weight materials through C_{10} and to oxygenated constituents of exhaust gas.

Since ozone formation is one of the principal indications of the extent of photochemical reactions in polluted air, a project was set up at the Armour Research Foundation to develop an instrument for continuous measurement of ozone in the atmosphere. A method of detection suitable for use in portable instruments was developed to determine ozone concentrations in the range found in polluted air. The principle of the method requires a catalyst upon which small concentrations of ozone are quantitatively decomposed. The rate of heat evolution, and consequently the catalyst temperature, is proportional to the ozone concentration. A patent assigned to the API has been applied for, and Mine Safety Appliances Company has been granted a non-exclusive license to use the method. Difficulties in circuit design and problems in the behavior of the catalyst at extremes of temperature and humidity have delayed final design of this instrument. The Smoke and Fumes Committee discontinued support of this project in 1956, but work has continued under U. S. Air Force sponsorship. Al-

though the principle of the method has been established, much work remains to design and develop a complete working system.

API-APF Cooperative Project

During the past two years, many organizations working on air pollution have placed considerable emphasis on the role of automobile exhaust in air pollution. Dr. W. L. Faith, in a paper presented at the Golden Jubilee Meeting of the Air Pollution Control Association in June 1957 [1], said,

> "No matter how you define it or which smog manifestation bothers you, you can find a relationship between smog and some constituent of auto exhaust — the aldehydes in exhaust stink; carbon monoxide is toxic and thus a health hazard; unburned gasoline and oxides of nitrogen can react under favorable conditions to produce eye irritation and to damage vegetation; and smoke from partially burned lube oil can easily restrict visibility and irritate the lungs in enclosed spaces."

In June 1957 the Smoke and Fumes Committee joined in a cooperative effort with the Air Pollution Foundation to study the effect of fuel composition on air pollution from automobile exhaust. This study, as well as the work of others, has shown that the problem of air pollution from automobile exhaust is extremely complicated. Many variables in addition to fuels need to be studied before any conclusions can be reached. The facilities at the Stanford Research Institute, designed to study eye irritation from irradiated auto exhaust and described in the Air Pollution Foundation Report No. 18 [2], have been teamed with the Franklin Institute mobile laboratory including the long-path infrared spectrometer located in South Pasadena to study this problem. Under the conditions investigated thus far, the exhausts from all fuels tested have shown similar air pollution manifestations.

Publications

Through its Publications Committee, the Smoke and Fumes Committee is making a continuing effort to publish the results of its sponsored research activities as rapidly as possible. Researchers are encouraged to appear on the platform at technical and scientific meetings and to publish their findings in the technical journals.

Since 1955 the Division of Refining of the American Petroleum Institute has held an annual technical session on air pollution in connection with its Midyear Meeting. Researchers from the various sponsored projects have appeared on the API platform to discuss their findings. In addition, Smoke and Fumes Committee sponsored research has been described at meetings of the American Chemical Society, at the Annual Meeting of the Air Pollution Control Association, and at the Annual Meeting of the Society of Automotive Engineers.

To date, the Smoke and Fumes Committee has spent approximately one and one-quarter million dollars to carry out this research program. The present rate of expenditure is about one-quarter million dollars per year.

Summary

In summary, may I again call to your attention the wide variety of research sponsored by the Smoke and Fumes Committee in the field of air pollution. The accomplishments of this committee include: (1) Research demonstrating that hydrocarbons and organic matter in the air react with oxides of nitrogen in sunlight to produce *smog* type air pollution characterized by its oxidizing ability; (2) Determination of the nature of many of the chemical reactions in the air leading to air pollution; (3) Studies of oxidant-type plant damage to determine the reactants and reaction products responsible for damage to vegetation from polluted air; (4) Experimental evidence that the oxidation of sulfur dioxide to sulfur trioxide in the atmosphere is too limited to produce significant reduction in visibility; (5) Tests to show that furnaces burning petroleum fuels do not release significant quantities of hydrocarbons to the atmosphere; (6) An analysis of the air in several United States cities showing absence of the abnormal ozone or oxidant content found in Los Angeles *smog;* (7) Analysis of the gaseous carbon compounds in the atmosphere to determine the source of atmospheric carbon; (8) Investigation of meteorological effects on atmospheric sampling to assist in planning and interpreting gas tracer tests.

In addition, the Smoke and Fumes Committee has been responsible for the development of outstanding new tools for air pollution research, including: (1) A successful technique to trace air pollution from a single source; (2) Gas chromatographic methods of analysis for the determination of the composition of exhaust gases; (3) A method of detection of ozone suitable for use in continuous, portable instruments; (4) The long-path infrared spectrometer and the associated techniques for use of the instrument.

Many problems remain unsolved, but the research program of the Smoke and Fumes Committee has contributed substantially to the basic knowledge of the sources, mechanisms, and methods of control of air pollution and has assisted materially in the development of new and better tools for the use of our scientists in the continuing effort to provide clean air for our nation.

(See Comments on following page.)

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COMMENTS

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The investigation of atmospheric pollution by stack gases in the Engineering Experiment Station of the University of Illinois is now in its thirtieth year. Many studies have been made of the reactions of combustion products in stacks and in the air, and of methods for removing the pollutants at the source. The results of all of the work are available to the public in bulletins of the Experiment Station and in papers in technical journals. In the co-operative research contract with the American Petroleum Institute it was found that the photochemical oxidation of SO_2 gas in air in intense sunlight was not fast enough to account for serious reduction in visibility. However, it was pointed out that different results might be obtained by oxidation in the liquid phase, such as in the droplets of a natural fog. Ellis (1931) found that the ratio of sulfuric acid to SO_2 in a London fog is higher than in fog-free air. A similar observation was made after a morning fog in an American city.

A Study Was Made

Accordingly, a study was made of the rate of oxidation of SO_2 absorbed from air by suspended drops containing manganese and iron sulfates, which are known to act as powerful catalysts for the oxidation reaction in solution. The results of the work indicated that the rate of formation of acid in a fog nucleated by particles of manganese sulfate in air containing 1 ppm. SO_2 might be as much as 500 times as fast as the photochemical oxidation in intense sunlight. This conclusion has been verified recently by measuring the rate of acid formation from dilute SO_2 — air mixtures containing fogs nucleated by very small particles of manganese and iron salts. The reaction proceeds in the dark and in light, and takes place when sodium chloride nuclei are also present, a condition that is apt to exist in the air of industrial cities even far inland from the sea coast.

The role of nuclei in other atmospheric reactions in air pollution is now being studied.