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SEVENTEENTH MID-YEAR MEETING
DIVISION OF REFINING

AMERICAN PETROLEUM INSTITUTE

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REFINING



SAN FRANCISCO, CALIF.

May 12 to 15, 1952

OPENING REMARKS OF THE CHAIRMAN TO THE SESSION
ON ATMOSPHERIC POLLUTION

H. G. VESPER *

This group session on atmospheric pollution is sponsored at this mid-year meeting by the Committee on Disposal of Refinery Wastes, which is one of the more active of the committees of the Division of Refining. I consider it a great privilege to be asked to be the chairman at this meeting, and believe it will be an interesting one.

At the outset I should like to repeat an announcement which has been made at one or two other places. This is that there has been one addition to the program. We shall have three papers as scheduled, and then promptly at 11:30 there will be the initial showing of a new colored film dealing with atmospheric pollution. This film has been made by the Stanford Research Institute on behalf of the Western Oil and Gas Association; and, although it is designed primarily for a non-technical lay audience, I believe you will find it extremely interesting from the standpoint of the subject matter of this session. The title of the film is "The Case of the Disappearing City"—certainly an intriguing title.

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With your permission, I shall make this announcement several times during the course of the meeting in order that those who may be coming in late or leaving will have an opportunity to come back at 11:30 and see this film.

It has been suggested that there has been perhaps too much emphasis on the general question of atmospheric pollution—in particular, smog—during recent months. It happens that this is the second group session on this general subject on the West Coast within the past several weeks. However, those of us who are particularly concerned with this subject, and who recognize its importance both technically and as a public-relations matter, certainly do not agree that it has been overdone. Sound, open discussion of its various phases is entirely appropriate and, in fact, very necessary, in order that we all have an intelligent understanding of the problems and their solution. Therefore, I believe that it is entirely fitting that this Division of Refining meeting have a session on atmospheric pollution, and I trust you will find it worthwhile.

SMOG: FACT AND FICTION §

PAUL L. MAGILL,* FREDERICK G. SAWYER,† AND RICHARD D. CADLE ‡

ABSTRACT

Many theories have been advanced to explain the cause of Los Angeles smog. Blame has been leveled against sulfur dioxide, the atomic bomb, the Mexican volcano Paracutin, butadiene, occult powers, the oil refineries, and many others.

The suggested smog cures have also been many and varied. Holes should be bored in mountains. Giant smokestacks built on the sides of hills could carry away the pollution. Dropping water from airplanes might also clear the air. These and many other "cures" have been suggested by sincere citizens. Other sincere citizens have been doing something about smog for many years. The Los Angeles Chamber of Commerce, the city and county health departments, and other groups made some progress in an early cooperative effort to abate air pollution. The problem was carried to the state level in 1947, when Assembly Bill No. 1 became law.

Since the activation of the Los Angeles County Air-Pollution Control District in 1947, industry in the county has spent more than \$17,800,000 for control equipment to reduce or eliminate emissions to the atmosphere and to meet regulations set up by the district.

The largest sums have been spent by the petroleum industry which, through the Western Oil and Gas Association, has spent, in addition, more than \$1,000,000 in research at Stanford Research Institute.

This study showed that combustion products comprised a major part of the total atmospheric pollution over Los Angeles. A survey in 1950 indicated that about 50,000 tons of fuel and rubbish were burned daily in Los Angeles County. Public and industrial burning of these materials emitted to the air each day at least 1,800 tons of combustion products. The present research program is a fundamental study of the atmospheric oxidant and its reactions with hydrocarbons in order to evaluate their contribution to smog.

Intelligent abatement of smog can only be brought about after research has given answers to many of the present questions. Funds must be provided for this research. A community can do it through use of tax funds, or it can be done by contribution from public-spirited organizations such as the Western Oil and Gas Association. The problem is complex, and will not be solved without support from all parts of the community.

There is a fiction that a million people can't be wrong. The fact is that they can be, and frequently are. Let us consider malaria, for example. The word means "bad air," which was originally believed to cause the disease. Inspired research by a few gifted persons showed that a mosquito—not bad air—was responsible for spreading malaria. Popular opinion finally bowed before knowledge of the facts.

Los Angeles has "bad air" of a sort. It has a polluted atmosphere, but so have many other cities. Perhaps we hear more about the Los Angeles problem because the famed California climate and polluted air are considered inimical. Perhaps it is just that Los Angelenos are better at publicizing their area, pro and con. The important point to consider is that a problem has existed for many years, and continues to exist.

Theories explaining the cause and cure of smog are legion. Many of the popular concepts have been as much in error as the original theory of malaria.

The fact that smog occurs intermittently has led many investigators to search during the daytime for obvious but sporadic emissions of pollutants, and to search the sky avidly at night when it was suspected

that some sly industries were disposing of their aerial waste.

The petroleum refineries have been blamed as being solely responsible for smog and its attendant eye irritation and reduced visibility. This idea was so firmly held that, even during a 6-week strike which shut down most of the oil refineries in 1948, the public could not be convinced that there had been no significant decrease in smog. Part of this attitude was probably generated from the view held by control authorities a few years ago. They blamed smog on sulfur dioxide, and the refineries were the largest emitters of the gas at that time. The oil industry then installed systems for recovering sulfur. At present a large part of the sulfur which formerly went to waste is being recovered. In spite of this, smog persists.

The production of butadiene in Los Angeles was believed by many to be the cause of eye irritation. People still complained of eye irritation long after the butadiene plants were closed down.

Some people have blamed smog on the Mexican volcano Paracutin; some have suggested the atom bomb; and still others have considered smog to be a manifestation of the occult.

The suggested remedies have been many and varied. Holes should be bored in the surrounding mountains to allow escape of the fumes. Giant smokestacks should be built against the sides of the hills to carry off the

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pollution. Fleets of high-flying bombers should drop tons of water mist to clear the air.

Hundreds of other smog cures have been offered. Clearly they have been the result of sincere thinking on the part of the people of Los Angeles who seek ways to rid their area of a nuisance. Unfortunately the average citizen is inadequately equipped, either by training or by information, to prescribe the cure for a problem as complex as Los Angeles smog.

History of the Effort

Many of the early citizens moved to Los Angeles in order to take advantage of the salubrious climate for relaxation and retirement. During the past few decades, however, the new settlers came to combine business with pleasure. They thought that a good place to live is also a good place to work. To provide the necessary goods and services for this expanding population, industry developed apace. With this human activity came the concomitant problem of waste disposal.

Visible air pollution became an official concern as early as 1909, when the Los Angeles Chamber of Commerce adopted a resolution calling upon the City Council to pass a smoke ordinance. An excerpt reads: "Smoke, which hangs like a pall over the city, makes an unfavorable impression on tourists and prospective citizens."

World War I came and went. Los Angeles continued to burgeon. The industrial winning of World War II added population and dirty air. By 1944 the public began to clamor against the polluted air, and the word "smog" was heard on many lips for the first time. Letters began pouring in to the civic authorities and to the Los Angeles Chamber of Commerce, which had invited industry to locate in the area.

About this time the Western Oil and Gas Association organized a public-health committee to study the waste problems of the oil industry, and to take whatever steps were necessary to influence member companies to prevent all unreasonable and unnecessary pollution of water and air. This committee, chairmanned by George J. Murray, Jr., of Tide Water Associated Oil Company, comprised plant superintendents and chief chemists.

A committee was also organized within the Los Angeles Chamber of Commerce in the latter part of 1944. This was known as the Air Pollution Committee (later the Atmospheric Purification Committee), and it also was chairmanned by Mr. Murray. This group now consists of 44 members, comprising representatives of the chemical-process and other industries, representatives of the governmental agencies such as the Los Angeles County Air Pollution Control District, the city and county health departments, the U.S. Weather Bureau, and several consulting engineers. The sole purpose of this committee is to develop and pursue a voluntary cooperative program between industry and civic authorities in an effort to aid in correcting air-pollution problems and to help solve the smog problem in the area.

Actively participating in the work of this committee from its inception was the Los Angeles City Health Department, under Dr. George Uhl, director. Much of this activity was carried out by Charles Senn, director of sanitation, and Major Harry E. Kunkel, in direct charge of air-pollution problems.

In the early stage of the air-pollution committee operation, a program was organized which provided for the obtaining of complaints of visible air pollution from citizens through local fire and police departments, as well as at the Los Angeles City Health Department and the Los Angeles Chamber of Commerce. At the bi-weekly committee meetings these complaints were discussed, and were divided among the committee members who would call upon the heads of various companies or organizations against whom the pollution complaints had been filed. Free engineering counsel was offered by the committee for solving these problems. A series of aerial surveys was also made, with the cooperation of the Civil Air Patrol, to study conditions in the area.

Late in 1945 the County of Los Angeles created a new office, that of air-pollution control director. I. A. Deutch was appointed to that position, and the Los Angeles County Air Pollution Control Department was activated. Recognizing that smoke and fumes were not necessarily confined within municipal boundaries, the department launched a program of contracting with the various municipalities for local surveys, inspections, and corrective measures. Municipalities were encouraged to adopt ordinances conforming with those of the county. The county offered to help solve local problems. The Los Angeles Chamber of Commerce endorsed this activity, and announced its willingness to cooperate with the municipalities in any way which would help.

While this county-city cooperative program was getting under way, the Los Angeles smog problem was carried to the state level when Assembly Bill No. 1, known as the state anti-smog law, was introduced and adopted at the 1947 session of the California state legislature. The act relates to the control and suppression of air pollution; provides for the establishment of air-pollution control districts co-extensive with county boundaries; and vests broad powers and authority in the law-enforcement agencies created thereunder.

While this state law was being drafted, a vigorous crusade was launched by the *Los Angeles Times*. A steady barrage of articles directed public attention to supposed culprits and current theories. This newspaper was a powerful factor in influencing public demand for immediate and drastic action in solving the smog problem.

The state anti-smog law, signed by the governor, June 10, 1947, became effective on September 19, 1947; and, after the required public notice and hearing, the Los Angeles Air Pollution Control District was created thereunder, October 14, 1947. A compulsory permit system was established almost immediately, and stringent rules and regulations governing various types of

emissions to the atmosphere were subsequently developed and adopted.

The year 1947 was also important in smog history because of additional activity in the Los Angeles Chamber of Commerce. A scientific committee was set up to advise industry and the community on scientific approaches to combat the smog problem. To supplement the work of this committee, a process consulting group was organized. Its primary function was to guide the various industry committees, and to bring to their attention possible remedial equipment for reducing emissions to the atmosphere. In addition, committees were formed within the chamber of commerce to study conditions in each of 13 industries in the area. A joint laboratory research group was also organized within the chamber to contract with industry groups for testing and experimental work. The California Manufacturers Association also has a waste-disposal committee which devotes its attention to air and water problems.

Since the creation of the Los Angeles Air-Pollution Control District in 1947, industry in the county has spent at least \$17,800,000 for control equipment in order to reduce or eliminate emissions to the atmosphere, and to meet the regulations set up by the district. A breakdown of this figure by various industries is as follows:

Industry	Amount Spent for Control Equipment
Petroleum	\$12,500,000
Gray iron foundries.....	2,000,000
Steel	1,400,000
Coffee	450,000
Brass foundries	350,000
Steel foundries and smelters.....	300,000
Lumber	300,000
Furniture	250,000
Fish	150,000
Paint	100,000
	<hr/>
	\$17,800,000

These and many other facts could be developed to show that industry has given close attention to the problem of air pollution in Los Angeles. Of specific interest to the petroleum industry have been the development and activities of the Committee on Smoke and Fumes within the Western Oil and Gas Association.

Western Oil and Gas Association

In December 1946 the presidents of the principal oil companies in the Los Angeles area appointed a committee to have the following general functions: *a*, to study the smoke and fumes situation in the Los Angeles area; *b*, to determine to what extent, if any, the refineries were contributing to the causes which resulted in poor visibility, eye irritation, and other discomforts; and, *c*, to develop what steps could be taken by the refineries to improve any undesirable conditions which might exist. The committee appointed at that

time comprised executives from Union Oil Company of California, Shell Oil Company, Standard Oil Company of California, Richfield Oil Corporation, Tide Water Associated Oil Company, General Petroleum Corporation, and The Texas Company.

At the first meeting, on December 11, 1946, the specific responsibilities assigned to the committee were outlined as follows:

1. To ascertain what smog is.
2. To determine to what extent, if any, the refineries are contributing to the smog problem.
3. To develop what steps should be taken by the refineries in order to get their own houses in order.
4. To compile all the evidence and turn it over to those in charge of public relations for the industry.

On April 18, 1947, an executive of the Independent Refiners' Association was invited to become a member of the committee.

The original title of the committee, "Petroleum-Industry Committee on Smog," was changed in February 1947 to "Petroleum-Industry Committee on Smoke and Fumes," and in October 1948 the committee became a part of the Western Oil and Gas Association as the "Committee on Smoke and Fumes."

At the very first meeting it was decided to approach the problem by assigning various phases of the investigation to different members of the committee, each of whom could draw upon the technical staff of the companies represented for assistance in the study of the subject assigned to him.

The assignments were:

1. To define smog, and to determine the components contributing to its formation.
2. To investigate the release of chemicals other than sulfur dioxide to the air by refineries and other industries.
3. To ascertain all sources from which sulfur dioxide was released to the air, with an estimate of the quantity of sulfur dioxide discharged to the atmosphere in each case.
4. To collect information regarding measures being taken by the different refineries to prevent the release to the air of undesirable emissions.
5. To develop what corrective methods should be adopted by the refineries to improve any undesirable conditions which might exist.

The subcommittee working on (1) was known as the Analytical Subcommittee, and its duties were defined as: The identification of those materials in the atmosphere which result in eye irritation, or reduced visibility. In the course of this investigation it soon became evident that one of the major problems of this group was the development of methods of sampling and analysis of sufficient accuracy to determine the quantity and nature of contaminants which were present in the atmosphere in very low concentrations but which, nevertheless, might be contributing to the unpleasant effects.

By March 1947 it was apparent that the problem assigned to this group was much more complex and extensive than had been at first anticipated, and that the coordination and direction of the work being done by the different companies would require far more time

than could be devoted to the matter by any member of the committee without serious interference with the performance of the duties for which he was responsible to his own company. It was, therefore, decided, at the meeting on April 16, 1947, to engage Stanford Research Institute to provide the following services:

1. Overall management, technical direction, and responsibility for the program.
2. The services of a full-time technical man to provide technological coordination of work presently being carried out at several sites.
3. An independent study to be conducted at Stanford Research Institute relative to the physiological response to lachrymators.
4. All of the necessary facilities and direction to assemble, correlate, and present in final report form the data as collected from the various scattered sources.

When Stanford Research Institute was engaged to take over the project, the work of the Analytical Subcommittee was coordinated with the work being done by SRI. Gradually more and more of the work was taken over by the SRI staff, so that the Analytical Subcommittee became inactive at the end of 1948.

The smog research program has continued at SRI. The scientific aspects of this program have been reported in technical journals, as well as in three interim reports. To date, this research program has cost the Committee on Smoke and Fumes about \$1,000,000. The continuing work is largely devoted to the fundamental aspects of air pollution.

In view of the possibility that the effluents from the various refineries might contribute to the contaminants responsible for the formation of smog and that other features of refinery operations might be obnoxious to the public, the Committee on Smoke and Fumes decided to undertake a study of current refinery practices to establish certain standards which could be observed in refinery operation without unreasonable difficulty or expense, and yet which would minimize any causes of annoyance by refineries to the public in general or to their neighbors in particular. The work of developing such standards was assigned to a subcommittee composed of representatives from Standard Oil, Shell Oil, Union Oil, Texas, Richfield, General Petroleum, Wilshire Oil, and the Socal Refining Company.

After about eight months of thorough study this subcommittee submitted its recommendations, which were embodied in a *Manual of Good Manners for Petroleum Refiners*. After approval by the Committee on Smoke and Fumes, this manual was printed by the Western Oil and Gas Association, and was made available to all interested refiners.

On December 14, 1949, Stanford Research Institute suggested establishing a smog consultants board consisting of scientists from California Institute of Technology, University of Southern California, and University of California at Los Angeles, who would meet periodically to discuss developments in the smog-research work, as well as plans for the future. This board has since been expanded to include scientists from all over the country, and they have been invited to

share their technical know-how in an all-out scientific effort to rid Los Angeles of smog.

Smog Research

More research and more kinds of research have gone into the Los Angeles smog problem than any similar community problem in the nation's history. It has had the benefit of the technical manpower and physical facilities of the best equipped universities and industries in California. A large part of the effort has been, and continues to be, directed toward understanding smog, because it was felt that a permanent solution of the problem could not be found until answers were found to the question: What is smog, and where does it come from?

The most extensive investigation to find answers to these questions has been sponsored by the Western Oil and Gas Association, and has been carried out at Stanford Research Institute. The results of this work have been presented to the public in three interim reports for the years 1948, 1949, and 1950.

The first interim report defined the problem. It showed that the eye irritation and poor visibility were at that time the chief disagreeable aspects of smog. It revealed that the climate had not changed, and that the population had undergone a relatively steady, though rapid, rate of growth before and during the war years. Industry had likewise expanded rapidly. The occurrence of smog was found to be controlled by various weather conditions, and a meteorological method for predicting the occurrence of smog was devised. A good start was made in developing laboratory methods for the analysis of the constituents of smog and for the testing of their eye-irritating properties.

The second interim report included a quantitative analysis of many of the contaminants in the Los Angeles atmosphere. The meteorological mechanism of smog was more thoroughly defined. Many of the materials responsible for the reduction of visibility were determined. Atmospheric particles studied included carbon, dust, mineral matter, droplets which were mostly water, and oil-like droplets. These latter droplets could have been produced by the slow oxidation and polymerization of some hydrocarbons in the atmosphere.

The second interim report stated further that at least nine substances capable of causing eye irritation had been identified in Los Angeles air. None of them was present in sufficient quantity to cause eye irritation by itself. However, human subjects experienced eye irritation when they were exposed to an artificial smog consisting of these nine substances mixed at concentrations found in Los Angeles air. Subsequent study showed that the gaseous substances, rather than the particles, were mainly responsible for the irritation.

The third interim report concluded that combustion products comprised a major part of the total atmospheric pollution over Los Angeles. A survey conducted in 1950 showed that about 50,000 tons of fuel and rubbish were burned daily in Los Angeles County.

Public and industrial burning of these materials emitted to the air each day at least 1,800 tons of combustion products, excluding carbon monoxide and carbon dioxide. Household burning of 4,000 tons of trash sent 550 tons of organic materials into the air every day. Approximately two-thirds of the chemicals which entered the air from combustion were organic in nature. Exhaust fumes from approximately 2,000,000 automobiles, buses, and trucks which drove an average of 50,000,000 miles per day added another 350 tons of organic substances, as well as 30 tons of aldehydes and 40 tons of nitrogen oxides.

A principal cause of reduced visibility was found to be air-borne droplets which were similar to those evolved by all combustion processes. The exact nature of these droplets, and the reason for their persistence in the atmosphere, were not known; but they comprised mostly water, and they evaporated slowly—probably because of a protective coating of some foreign material.

As the work continued into 1951, it became apparent that a more detailed and fundamental study of several aspects of smog was required. One of the most perplexing features of the Los Angeles atmosphere has been the observation that a high concentration of a strong oxidizing substance resembling ozone was found whenever smog was severe. This confirmed some previous observations by rubber companies in the area. A study of rubber-tire cracking in various cities of the United States had shown that Los Angeles was among those places where ozone cracking of rubber was most severe. Whether abnormally high concentrations of ozone were present in fact has been questioned by many investigators, inasmuch as other oxidizing agents such as peroxides, nitrogen oxides, and nitric acid have been found in Los Angeles air.

During the past year substantial evidence has been obtained that at least a large part of the oxidant is ozone. The reason for its occurrence is not yet known. Various theories have been advanced. The oxidant may be considered as being of natural origin, being brought down from the upper atmosphere. It has also been considered as being formed by photochemical action of the sun on atmospheric impurities. The oxidant may also be due to some unknown electrical phenomenon relating to charged particles in the atmosphere. Much more work remains to be done before this aspect of the problem can be clarified.

A. J. Haagen-Smit,^{1a} of the California Institute of Technology, has observed that, when high concentration of ozone and olefin vapors are mixed, they react to form aerosols. He has suggested that such reaction products are important constituents of smog.

Research during the past year by Stanford Research Institute indicates that ozone reacts very rapidly with olefins at concentrations which could exist in smog to form complex products which decompose rapidly to form aldehydes, dialkylperoxides, and high molecular-weight organic materials. A mixture of these reaction products was prepared at concentrations believed pos-

sible in the Los Angeles atmosphere. Human subjects exposed to these materials experienced little or no eye irritation.

Concurrent with the research sponsored by Western Oil and Gas Association at Stanford Research Institute, work was carried out at the California Institute of Technology, sponsored by the Los Angeles County Air-Pollution Control District. The results published to date pertain largely to the effect of hydrocarbons and their oxidation products on growing crops. Farmers in the Los Angeles area have noticed that, associated with smog attacks, injury has appeared on certain leafy vegetables, such as spinach, endive, lettuce, beets, and Swiss chard.²

According to Haagen-Smit et al.³: "The reaction products of ozone with unsaturated hydrocarbons produced typical smog damage on all of the indicator plants. The damaging factor must, therefore, be attributed to the peroxides formed in the ozonization process. Optimum effects were obtained by using olefins with five and six carbon atoms with the double bond in the end position. However, the end position of the double bond is not essential, since 3-*n*-heptene, 4-*n*-nonene, and cyclohexene gave typical smog damage upon ozonization. The concentration of ozone at which damage occurs with the olefins is well within the range of ozone concentration found in the atmosphere as determined by the rubber-cracking test. The optimum activity of the C₅ and C₆ series is attributed to the stability of the intermediate products in the reaction process. The catalytic oxidation of the olefins with NO₂ under the influence of sunlight produces oxidation products very similar to those produced by ozone. In the plant fumigations with oxidation products of olefins, lachrymatory effects were often observed."

In addition to its research contracts with several universities, the Los Angeles County Air-Pollution Control District maintains its own research staff to identify pollutants in the atmosphere for such contaminants as sulfur dioxide, sulfuric acid, aldehydes, and particulate matter.

Future Smog Research

The questions may be reasonably asked: "Why do further research?" and "Don't we have sufficient data available now to enforce the law and jail or fine anyone who pollutes the air?" This approach is sponsored by so many persons that it deserves a fair answer.

Industry has received a large share of the blame for smog. Part of the reason for this is that the average person considers industry as being inanimate. It is a collection of steel, stone, and mortar. Certainly these objects have no feeling for the community. Also, a company is big and rich. It should be able to afford spending limitless sums for erecting smoke-recovery and similar devices. These ideas are just not correct.

The company is made up of people. Those who are designated as management are also individuals of the community. They too dislike smog. They are willing to do their part, but they cannot spend company funds

^a Figures refer to REFERENCES on p. 291.

for recovery equipment unless it can be shown that the factory discharges cause nuisance or contribute to smog. All too often the company is forced to install expensive equipment when nobody really knows whether it will help the smog problem or not. This sometimes makes it difficult for a management to maintain operations, sell in a competitive market, and show a profit. At the same time, as a part of the community, the company must maintain the good will of the public. Most firms are trying to be good neighbors. They are doing their part in reducing the quantity of pollutants being discharged to the atmosphere.

The individual citizen is also a polluter of the air. His backyard incinerator, his automobile, and his heating unit all pour forth products of combustion which contribute to smog. Changes must be made in these devices so that they will not pollute the air. But what changes should be made? And how? Only research will give the answer, but research costs money. Ideally, the cure for smog should not cost the individual money or personal inconvenience. This appears to be an impossible goal.

Another phase of smog which will cost money is a complete study of its effect on health. So far no research has been conducted which shows that Los Angeles smog is harmful to human health. Perhaps one reason is that practically no medical research has been done.

Some people ask whether the average smoker of cigars, cigarettes, and pipes is exposed to more polluted air than that from smog. For many years medical men have debated the effects of smoking on health. Many more years will pass before the health effects of smog can be determined.

Through one means or another, answers to all of these questions must be found through research. Funds must be provided. A community can do it through use of tax funds, or it can be done by contributions from public-spirited organizations. The Western Oil and Gas Association is an excellent example of the latter. So far it has been the principal contributor to research on smog. It would seem unfair to expect these private donations to continue without more assistance from other parts of the community.

ACKNOWLEDGMENT

The authors wish to thank Messrs. George J. Murray, Jr., of Tide Water Associated Oil Company, and Jerry Luboviski, of the Western Oil and Gas Association, for their assistance in making available many of the data included in this paper.

REFERENCES

- ¹A. J. Haagen-Smit, *Eng. Sci. Monthly (Calif. Inst. Technol.)* 14 [3] 7-13 (1950).
- ²J. T. Middleton, J. B. Kendrick, Jr., and H. W. Schwalm, *Plant Disease Repr.* 34, 245-52 (1950).
- ³A. J. Haagen-Smit et al., *Plant Physiol.* 27 [1] 18-34 (1952).

DISCUSSION

Harry Levin (The Texas Company, Beacon, N. Y.):
First I should like to congratulate the authors for com-

pressing into a relatively short paper a large amount of experience and experimentation. It is understandable that those who are exposed to smog and those who are accused of causing it should become impatient for a solution; but, as one who has done a little work in this general field, I should like to make a plea for patience on behalf of the investigators.

The problem is very complex; and, before this very extensive investigation was initiated in the California area, there had really been very little information in the literature on this general subject. I believe the authors and the other workers in this field have made a great deal of progress in establishing the probable or possible nature of smog.

I say "possible" because I am not entirely convinced that these are the real causes. I believe what has actually been demonstrated by the many workers in the field are things which could be causes. As the knowledge of the causes increases, we can certainly expect that the solution will be much nearer at hand.

As a result of the investigations which have been made in the California area, I believe that there has been introduced a new concept of pollution. In the past I believe we were content to assume that the objectionable constituents of the atmosphere—the obnoxious and the irritating ones—were introduced *as such* into the atmosphere. More recently it has been indicated that a normal and, in itself, not too objectionable a constituent in the concentrations in which it naturally exists, viz., ozone, combines in the atmosphere with another relatively harmless constituent in the concentrations in which it exists, viz., the hydrocarbons, for which the oil industry has at least in part been blamed. These two harmless and unobjectionable constituents combine to produce the bad one—the irritating and obnoxious constituent.

This new concept leads to several interesting implications, and it is in this connection that I have several questions for the authors.

The petroleum industry in this area has spent a great deal of money to recover sulfur from some of its product gases in order that the subsequent combustion products of those gases will contain less sulfur dioxide and, hence, a great deal less sulfur dioxide is introduced into the atmosphere. Because ozone, which is alleged to combine with hydrocarbons to give evil-smelling and otherwise objectionable constituents, is a powerful oxidizing agent, and as sulfur dioxide is a powerful reducing agent, the question is raised whether this reduction of the sulfur dioxide in the atmosphere should not actually make the condition worse—inasmuch as, by removing it from the atmosphere (by not introducing it into the atmosphere), there is present a larger excess of ozone to combine with hydrocarbons and make objectionable constituents.

That is question No. 1; i.e., whether there is any evidence on this point. Would you care to answer the first question, Mr. Magill?

Mr. Magill: I believe that is a very interesting question, and it is one about which we have been thinking

for some time. Until we know a lot more about where the ozone comes from, I believe we have to be a little careful when the question is considered. It has been proposed that the sulfur dioxide is one of the causes of ozone. On the other hand, we do know that, in the laboratory, ozone and sulfur dioxide do react so slowly that we are inclined to suspect that removal of the sulfur dioxide may not make too much difference.

Mr. Levin: Would you expect that the ozone and sulfur dioxide would react more slowly than ozone and hydrocarbons?

Mr. Magill: Yes, they do—very much more slowly.

Mr. Levin: The other question again relates to the possible contribution by hydrocarbons. If the hydrocarbons react with ozone to produce these objectionable constituents, you might expect that over any given interval of time—say, eight hours—these objectionable constituents would increase in concentration at the expense of the hydrocarbons. Is there any information on that point?

Mr. Magill: The effect of the hydrocarbons is one of the things we are also studying. The simple fact of the matter is that, in the concentrations upon which we are working, we don't know how to measure hydrocarbons as distinguished from other materials which might be formed. Therefore, I believe the evidence is non-existent at the moment.

Mr. Levin: I take it from that, then, that one shouldn't be too hasty in concluding that the hydrocarbons are at fault merely because they are present simultaneously?

Mr. Magill: We shouldn't be too hasty, I agree with you.

George R. Lake (Union Oil Company of California, Brea, Calif.): I also should like to compliment the authors on doing a very good job of summarizing the air-pollution picture as it exists in the Los Angeles Basin. The question I should like to ask the authors concerns some of the cost figures; i.e., their figures of about a million dollars for Stanford Research Institute work, and about \$13,000,000 for the petroleum industry. Was the \$13,000,000 expenditure limited to equipment for the control of emissions?

Mr. Magill: I believe they were. Those are the figures which were given to us as being the overall expenditures for air-pollution control.

Mr. Lake: I suspected they were. Therefore, I should like to point out to you that \$13,000,000 represents only a small part of the industry money which is going into the air-pollution work. You must realize that, in addition, there are many committees—some of which were mentioned by Mr. Magill and some of which are now being organized in the petroleum industry—which are spending many man-hours working on this problem. Furthermore, most companies have air-pollution experts who spend part or all of their time in controlling emissions from the refineries and in insuring that new installations will not introduce additional contaminants into the air. Many companies also are carry-

ing on rather extensive private investigations of their particular air-pollution problems. Therefore, it is evident that the petroleum industry is putting into this work a tremendous amount of money.

The second point I should like to make is that, unless we make use of the findings of these research institutes, as well as of the committees and of the individual company efforts, by publicizing them, we are failing to take advantage of all the values which have been obtained by the research work.

Some of you may have attended, last week, the Second National Air Pollution Symposium at the Huntington Hotel in Southern California—at which time Mr. Manchester Boddy, one of the prominent publishers in the Los Angeles area, pointed out that the great need of the newspaper people is for someone to take the findings of these various groups and to translate them into words the layman can understand. He pointed out that much of the unfavorable publicity which had been obtained for the oil industry was the result of the translations done by newspaper people who had not realized the exact meaning of some of the findings.

Therefore, may I urge that all of us make it a point to be interpreters of these data ourselves, to pass them on to our friends, and to do everything we can to see that newspapers get correct interpretations.

C. H. Bunn, Jr. (Standard Oil Development Company, Linden, N. J.): It is undoubtedly a fact that Los Angeles has smog. Fiction comes into the picture with some of the suggested sources and cures. I do not propose right now to further the controversy concerning the several suggested causes of smog but, rather, to probe the relationship between the unpleasant conditions frequently experienced in Los Angeles and air pollution as it exists at other locations in the country.

I believe most students of the problem agree that the semi-circular mountains, coupled with the meteorological conditions, form a natural caldron for collecting and concentrating all of the local air pollution. This situation, if not unique, is at least a very special aspect of the Los Angeles problem. I believe that it would be difficult to find another large center of population where the enveloped air is held in place for three or four days without any widespread dispersion. The time element thus provided is probably an important factor, in that it permits intimate contact and chemical reaction between the relatively mild contaminants.

Now the question I should like to ask Mr. Magill is this: Is the severity of Los Angeles smog due only to the special geographical and meteorological conditions which exist there, or are there other unusual sources primarily responsible for its concentration? In short, do we have incipient smog, with its ultimate discomforts, at other cities—thus making the basic problems similar?

Mr. Magill: As I mentioned, Los Angeles is unusual in that it has 260 days of the year of inversion. To our knowledge, there are no other cities just like this. You ask the question: May there not be incipient

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smog such as we have in Los Angeles, and I believe the answer is "yes." We made a survey at one time because we were interested in answering this question. We asked questions of health departments in major cities—most of them with a population of more than 100,000—and about 30 per cent of them had instances of eye irritation recorded. And, if any of you happened to be at the meeting of the American Chemical Society in New York at the time of its air-pollution symposium, you will remember that there were a considerable number of comments to the effect that the city of New York is just like Los Angeles. It is warm there; there is eye irritation; and it is hazy.

Therefore, I believe there are other places which have that condition. But the difference between Los Angeles and other places is one principally of topography and meteorology.

Chairman Vesper: I believe Mr. Bunn's comments and Mr. Magill's answer point up something very important which all of us should realize, viz.: that, although this smog problem is perhaps localized and given regular publicity in terms of Southern California and the Los Angeles area in particular, it does represent something which is of concern to all of us who are connected with major metropolitan areas.

We here in Northern California are inclined to talk about our Southern California neighbors in various ways. In particular, we like to make "comments" about Los Angeles. The subject matter of this discussion this morning—the question of smog—as presented in the paper and the discussion thus far, offers an opportunity to carry this forward.

Donald L. Campbell (Standard Oil Development Company, Linden, N. J.): As one who has worked with Mr. Bunn on air-pollution problems, I should like to ask his permission to supplement what he has said—

particularly with regard to a question which came up yesterday in a meeting which he was unable to attend. In that other meeting a question was raised about a process put forward by the Standard Oil Development Company, with particular regard to a byproduct stream which contains some sulfur dioxide. As the main object of the meeting yesterday was the process itself, the answer given simply was that, in this basic process design, no provision had been made for the elimination of the sulfur dioxide from this byproduct stream.

As we are concerned this morning with another aspect of it, I should like to amplify that point by saying that, in the group which designs the refineries for the Jersey interests, a great deal of attention is paid to air pollution, and that the basic design of this equipment is studied further, i.e., beyond the requirements of the process, to see whether it is necessary to remove such chemical compounds from byproduct streams.

The first question is whether this particular byproduct is in kind and in quantity such as to cause real difficulty in a neighborhood; and the second question is what is the neighborhood? Obviously, there is a different answer, depending on whether a refinery is to be built on a breezy hill far removed from any city, or in a valley adjacent to some very large metropolis. Therefore, the basic design is made without provision for removing these byproducts, and then a separate study is made as to whether it is desirable to do so.

But what I should like to emphasize is that the company—and I believe I am speaking for the industry—is really making a very sincere effort to study each and every one of these byproduct streams to see what can be done about them.

Chairman Vesper: It is quite clear that this matter of smog, and its causes and its effects, have many facets. Some of the more unusual and controversial of these are the subject matter of the second paper for presentation this morning.

THE POLICEMAN IS COMING!

VANCE N. JENKINS *

ABSTRACT

This paper develops the thesis that the policeman is coming to check on the air-pollution activities of the petroleum industry—not as a result of a large or sudden increase in air pollution in refining centers of the industry, but as the result of the bringing forth of a new and as yet unproved theory regarding the nature and cause of air pollution in such areas. This theory, developed by Dr. A. J. Haagen-Smit of the California Institute of Technology, proposes that the bluish-colored, visibility-reducing, evil-smelling, eye-irritating, allegedly crop-damaging type of air pollution, known as smog in the Los Angeles area, is composed of the reaction products of the vapors of primary olefins having 5 to 7 carbon atoms with the oxidant, presumably ozone, known to

At the Sixteenth Mid-Year Meeting of the Division of Refining in Tulsa a year ago Mr. W. L. Stewart, Jr., gave an address entitled "Laws, Morals, and Manners." In this address, which dealt with the air-pollution situation in the Los Angeles area and the part the petroleum industry was playing in its investigation, he made a very prophetic statement. He said . . . and I quote: "I think it would be very wise to know more about our problem, as well as the overall problem of air pollution, than the policeman—because he is coming, believe me."

Events occurring since Mr. Stewart made this statement tend to indicate that not only is the policeman coming, but that he may arrive much earlier than the petroleum industry expected him. And, strangely enough, his early arrival probably will not be caused by any large or sudden increase in air pollution in or around the producing or refining centers of the industry. It probably will occur as the result of a new and as yet unproved idea—a new theory—a new way of thinking with respect to the possible cause of the present air-pollution situation in certain areas.

The fact that this new idea is still merely a theory—a plausible but entirely unproved speculation or guess—will make no difference. Imagination and suspicion are often responsible for the whistle being blown for a cop. And the fact that any evidence against the suspect may be purely circumstantial does not in any way tend to lessen the severity of the charge which may be filed against him. The suspect may be inconvenienced greatly, both personally and financially, by the proceedings. But, under the ordinary American system of jurisprudence, he eventually has a day in court where the charge against him must either be proved beyond a reasonable doubt to a jury of his peers or he must be judged innocent and allowed to go free. It is true that under this

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exist at times in relatively high concentrations in the Los Angeles atmosphere. This paper discusses the theory in detail—pointing out that so far it is unproved, and citing various objections which have been raised against it. Possible sources of unsaturated hydrocarbon vapors which are present in the air are discussed, and indications of the possible amounts which may arise from different sources are given. The warning is voiced that, unless the Los Angeles County Air Pollution Control District takes a more realistic view of the relative amounts of such hydrocarbons contributed to the atmosphere by automotive exhausts and by evaporation from refineries, the policeman will soon have his hand on the shoulder of the petroleum industry in Los Angeles County.

system an innocent suspect is sometimes judged to be guilty of the charge brought against him. This happens very seldom, however; and, when such a case is discovered, restitution usually is made insofar as it is possible to do so.

The Law

Unfortunately, however, when the cop is called in about an air-pollution matter, the proceedings which ensue usually do not follow the ordinary American system as set forth previously; for the party who summons him is usually from an air pollution control bureau or department which, as such, ordinarily is a political agency which governs by decree. For example, allow me to read from California Assembly Bill No. 1 enabling the creation of air pollution control districts in the state of California. Art. 4 of this act reads in part as follows:

"The air pollution control board of an air pollution control district may make and enforce all needful orders, rules, and regulations necessary or proper to accomplish the purposes of this chapter for the administration of such district, and may perform all other acts necessary or proper to accomplish the purposes of this chapter Whenever the air pollution control board finds that the air in the air pollution control district is so polluted as to cause any discomfort or property damage at intervals to a substantial number of inhabitants of the district, the air pollution control board may make and enforce such orders, rules, and regulations as will reduce the amount of air contaminants released within the district."

The same bill provides for the appointment by a district's air pollution control board of a three-man hearing board before which a party may demand a public hearing of his appeal from a ruling of the control board regarding his application to build or operate a device specified by the regulations, the use of which may cause

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the issuance of air contaminants. But the hearing board is not consulted regarding the validity of ideas upon which the control board bases its decisions. Therefore, these may be based upon plausible but unproved speculations, such as the interesting one hinted at previously herein or the former one concerning the starring rôle sulfur dioxide was supposed to play in Los Angeles smog formation.

The Sulfur-Dioxide Fable

I am sure you all remember the sulfur-dioxide fable. It has been told so many times. How black smoke and sulfur dioxide had been going steady for years in air-pollution circles in the soft coal-burning cities; how, when sulfur dioxide vanished, the black smoke just wasted away and visibility improved overnight; how the initial program of the Los Angeles County Air Pollution Control District was concentrated on reducing black smoke and sulfur-dioxide contaminants as a sure cure for the city's smog; how, in cooperating with the district in this program, the oil refiners spent a lot of money taking hydrogen sulfide out of their fuel gases in order to prevent sulfur-dioxide formation; and how now that air pollution from sulfur dioxide and black smoke has been so greatly reduced that we have even more and thicker smog. And there are some who say that the removal of the sulfur dioxide may have helped make it worse.

The New Idea

Well the new idea—the new theory—is considerably more complicated than the sulfur-dioxide one. This makes it considerably harder to prove or disprove, and that is why I want to tell you about it and warn you against believing all the publicity releases you may see about it. For it is merely an unproved speculation at this time—an interesting guess which apparently has been seized upon by the Los Angeles County Air Pollution Control District as a means of gaining favorable publicity for its efforts at the expense of bad publicity for the petroleum industry. But the fact that the idea is unproved, that it is a mere theory, will not keep it from costing the petroleum industry a lot of money for the prevention of the escape of vapors which may be proved later to play no part in causing smog.

The new, unproved idea is that smog—the visibility-reducing, evil-smelling, eye-irritating, and allegedly crop-damaging type of air pollution frequently present over Los Angeles—is caused by the oxidation in the atmosphere of certain low-molecular-weight unsaturated hydrocarbons or olefins which escape by evaporation from refining and marketing installations of the petroleum industry. This theory—this speculation—is based on work done by Dr. A. J. Haagen-Smit, professor of biochemistry at the California Institute of Technology.

Dr. Haagen-Smit is a first-class scientist, and one of my most highly valued acquaintances. Somewhat over two years ago he became intensely interested in the crop-damaging aspects of Los Angeles smog—so in-

terested, in fact, that he took a leave of absence from his teaching duties and devoted all of his time to developing his ideas on the cause of plant damage by smog and the nature of smog.

Ozone May Play a Part

From work done earlier by Dr. A. W. Bartel of the U. S. Rubber Company on the rubber-cracking phenomenon peculiar to the Los Angeles area, it was known that ozone, or an oxidant having the oxidizing properties of ozone, is at times present in the Los Angeles atmosphere in concentration many times higher than that in which it is found in other locations. Dr. Haagen-Smit theorized that this oxidant reacted with the vaporized unsaturated hydrocarbons present in the atmosphere to form ozonides or peroxides. He then went a step further and speculated that these reaction products or polymers of their decomposition products persisted in the atmosphere in the form of very small droplets or aerosols, and that they were responsible for most of the reduction in visibility, the odor, the eye smarting, and even some crop damage claimed to be experienced during smog periods.

Working in a plexiglass chamber in the laboratory, he was able, under certain conditions, to produce visible mists or aerosols by the reaction of ozone and selected olefinic hydrocarbons. These aerosols were claimed to have the characteristic odor and eye-irritating effect of natural smog. He claimed to find that severe plant damage was not caused by the reaction products of ozone and just any unsaturated hydrocarbon vapor. The hydrocarbon had to be one of three primary straight-chain olefins—one of those having from five to seven carbon atoms with the double bond at the end, the worst offender being normal 1-hexene. Smog-sensitive plants such as spinach, endive, and beets were said to develop typical smog-type damage after exposure to aerosols formed by reaction of these hydrocarbons and ozone.

Possible Rôle of Nitrogen Dioxide

Dr. Haagen-Smit did not believe that all of the oxidant necessary to form the amount of olefin reaction products which, according to his theory, would be required to make natural smog could be ozone of normal meteorological origin. Therefore, he sought for another explanation of its origin, and found a possible one proposed by Dr. Francis E. Blacet of the Department of Chemistry of the University of California at Los Angeles.

Dr. Blacet advanced the idea that nitrogen dioxide (NO_2) is formed in the Los Angeles atmosphere by the oxidation of nitric oxide (NO) which, in turn, is formed in small amounts from the nitrogen and oxygen of the air during the high-temperature combustion of all ordinary fuels. He suggested further that, after the nitrogen dioxide had formed, it was decomposed photochemically by sunlight to yield nitric oxide—from which it had been made originally—and an active oxygen atom. The regenerated nitric oxide is thus supposed to be made

available for re-entering the oxidation-reduction cycle, whereas the active oxygen atom either may combine with an oxygen molecule from the air to form ozone or enter directly into oxidation reactions. Dr. Blacet gave a paper on this suggested reaction mechanism last year at the air-pollution symposium held in New York in connection with the XIIth International Congress of Pure and Applied Chemistry.

Some Disagree

Following up this idea, Dr. Haagen-Smit exposed plants to ultraviolet light in an atmosphere containing small amounts of nitrogen dioxide and olefins, and obtained damage which he claimed was similar to that produced by natural smog. There are some, however, who do not believe this experiment proves ozone was present for the reason that, under the influence of the ultraviolet light, the nitrogen dioxide may have reacted directly with the olefins to produce plant-damaging compounds.

In fact, there are those who reject the entire idea of ozone formation by the mechanism proposed by Dr. Blacet. They point out that, at atmospheric temperatures, pressures, and oxygen concentrations, the oxidation of nitric oxide to nitrogen dioxide is a very slow reaction and would not be expected to go very far during the relatively short duration of a smog period. They also do not understand why, if sunlight and nitrogen oxides are involved in its formation, the ozone or oxidant concentration in the Los Angeles atmosphere is sometimes found to be quite high at night—or why it is sometimes found to be quite high in the desert, and in the mountains above the smog layer where nitrogen-oxide concentrations are quite low. There is among this group a general feeling that at least a portion of the oxidant is ozone which has been transported by meteorological processes from the ozone layer in the lower regions of the stratosphere.

Likewise there is a distinct lack of unanimity of opinion among scientists regarding the extent to which ozone-olefin reaction-product aerosols resemble the odoriferous, eye-smarting constituents of natural smog. For example, I associate two entirely different odors with Los Angeles smog. Occasionally it has a very sweet, almost floral, fragrance. More often, however, it smells exactly like the back end of a public bus, such as one gets stuck behind all too frequently in Los Angeles traffic. My eyes are very sensitive to the exhaust from these buses as well as to the lachrymator in natural smog. To me, the ozone-olefin synthetic smog aerosols have a not unpleasant, sharp, terpene-like odor, very different from that of smog, and they do not hurt my eyes.

The Stanford Research Institute, which has been working on the Los Angeles smog problem for the Smoke and Fumes Committee of the Western Oil and Gas Association for four years' time—and for a little more than a million dollars—does not believe that ozone-olefin aerosols contribute materially to the reduction in visibility which accompanies a Los Angeles smog period.

The institute finds that, if ozone and low-boiling olefins are brought together in concentrated form—as, for example, by leading ozone into a small-diameter glass tube through which a stream of the hydrocarbon vapor is flowing—a dense fog or aerosol will be formed. This is the method of mixing used by Dr. Haagen-Smit in most, if not all, of his experiments. On the other hand, it is found that, if ozone and olefin vapors at reasonable concentrations—such as those which might exist in a highly polluted atmosphere—are allowed to diffuse or mix together, as would occur in the air, no mist or aerosol forms and, hence, no reduction in visibility occurs.

In both Dr. Haagen-Smit's articles and talks he has been careful to point out that there are several sources which might supply the hydrocarbons he considers necessary to smog formation. Among them he lists inefficient furnaces, garbage burners, automobile exhausts, and petroleum producing, refining, and marketing activities. He even goes so far as to say that, if the Los Angeles Basin were covered with its original sage brush instead of with more than 4 million people, 2 million automobiles, and a million backyard incinerators, the air would still be polluted with about 50 tons of hydrocarbons per day as the result of the evaporation of the essential oils from the sagebrush foliage.

Estimated Vapor Loss

The Los Angeles Air Pollution Control District has not been so broadminded. It insists that only one source of unsaturated hydrocarbons is of any importance, viz., cracked gasoline evaporating from the refining, shipping, storage, and marketing facilities of the petroleum industry.

Last October Colonel Gordon P. Larson, director of the district, made an official estimate of the hydrocarbon-vapor losses of the petroleum industry in the Los Angeles area. This estimate, which did not include losses from crude-oil production, was considerably lower than his previous ones, but it was still a sizable figure, viz., 920 tons per day. This is equivalent to about 7,360 bbl per day, or 2,686,400 bbl per year. This total was broken down into 2 sub-totals, viz., one of 800 tons per day which it was estimated was lost from refining operations and storage tanks, and another of 120 tons per day which it was estimated was contributed by gasoline shipping and marketing operations at refineries, ocean and bulk terminals, and retail filling stations.

A further breakdown of these figures indicated that it was believed that 16 per cent, or 130 tons per day, of the refining and storage losses consisted of unsaturated hydrocarbons; whereas only 15 per cent, or 18 tons per day, of the gasoline shipping and marketing losses were said to be unsaturated hydrocarbons.

These are very interesting figures. They are interesting because of the fact that, in the absence of accurate substantiating data, it is very difficult for one familiar with refining operations and gasoline compositions to see how the percentage of unsaturates in the total hydrocarbon-vapor losses from refining and storage operations can be greater than the percentage of un-

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A still further breakdown of these values indicated that 37 per cent, or 48 tons per day, of the unsaturated hydrocarbon losses from refining and storage operations and 95 per cent, or 17 tons per day, of the hydrocarbon losses from gasoline shipping and marketing operations consisted of olefins having only 4 to 6 carbon atoms per molecule. This is a total of 65 tons per day of 4 to 6 carbon-atom olefins which the estimate indicates is lost to the air each day by the petroleum industry in the Los Angeles area. These figures are interesting because of the singling out of the 4 to 6 carbon-atom olefins as the real offenders. This marks a departure from the views of Dr. Haagen-Smit who included the primary olefins having 7 carbon atoms, but not those having only 4, in his original list of smog-forming suspects.

Whether the actual magnitude of the hydrocarbon-vapor losses estimated to occur in the Los Angeles area by Colonel Larson represents a realistic value is another question. Some are emphatic in expressing their views that this is not the case.

Likewise there is considerable question in the mind of quite a number of people as to whether—assuming for the moment that the Haagen-Smit theory is correct—the 65 tons per day of 4 to 6 carbon-atom olefins estimated by Colonel Larson to be lost to the air by the petroleum industry in the Los Angeles area could account for the eye-irritating, tear-producing properties of Los Angeles smog—even if completely reacted with ozone. This group argues that it is well-known that the primary reaction products of primary olefins and ozone—the ozonides and peroxides—are unstable and decompose readily and rapidly to form aldehydes, organic acids, rather inert dialkyl peroxides, and other substances. The total weight of aldehydes—the most eye-irritating reaction product—formed is somewhat less than that of the original olefins subjected to oxidation. They point out that Dr. Haagen-Smit in his original article estimated 400 tons of formaldehyde would have to be contained in the 25-mile-square, 1,000-ft-deep smog layer to render it irritating enough to produce tears. In view of this figure, they do not understand all the concern over the estimate of 65 tons of unsaturated hydrocarbons contributed by the petroleum industry when it is known—not estimated—that at least three or four times that amount is contributed by automotive exhausts.

Example of Known Vapor Loss

On the other hand, we should not lose sight of the well-known fact that, unless sufficient care is taken to prevent its occurrence, it is possible for relatively large amounts of petroleum hydrocarbons to be lost by evaporation during certain operations or from certain types of installations. For example, I have at hand data from a detailed study of the evaporation losses occurring from a refinery waste-water skimming-pond system. Over a 3-week period this system lost an average of 240 bbl per day of hydrocarbons by evaporation and

recovered an average of 740 bbl per day of 33.6-deg-API-gravity oil.

During this interval of time samples of the entering oil were taken every two hours. Recovered oil was pumped to storage only during the day shift, and during this time pump samples were taken every hour. Daily composites were made from each group of samples, and weekly composites were then made from the daily ones. The weekly composite samples were subjected to thorough fractional distillation. An analysis of the data obtained indicated that 23 per cent—220 bbl per day—of the entering oil was lost by evaporation while it was undergoing recovery in the skimming ponds. A study of the vapor outlets of the sewer system revealed that an additional 20 bbl per day of very light constituents, such as butane and pentane, was being lost before the waste water reached the skimming ponds. Thus an average of 240 bbl per day—about 30 tons per day—of hydrocarbons in the gasoline-naphtha boiling range was lost by evaporation from the waste-water disposal system of the refinery during the three-week period of the study.

This case history of known losses from a waste-water disposal system is not given in order to make the point that slightly less than 1 ton per day of the vapors lost consisted of olefins having 4 to 6 carbon atoms to the molecule—and thus to suggest that the petroleum industry need not worry about the implications of the Haagen-Smit theory of smog formation. On the contrary, it is cited in order to cause you—the representatives of the petroleum industry—to pause and consider the real magnitude of the industry's vapor losses, and how little you may know about those occurring in your own plant.

The 240-bbl-per-day loss just cited is equivalent to 87,600 bbl per year. Now this is a lot of gasoline, and it is worth a lot of money. An equal or larger amount may easily be lost from a relatively small rundown tank at a thermal or catalytic cracking plant if proper precautions are not taken. And a lot more than one ton per day of that type of loss would consist of olefins.

Similarly, substantial losses may occur from blowdown stacks, from storage, during unit shutdown operations, from vacuum jet exhausts, and from many other sources at refining and marketing installations. Their total might astonish you. Fortunately, the normally liquid portion of the escaping vapors is worth real money; and, hence, if the amount of vapor loss occurring is sufficient to result in an air-pollution problem, the economics of its recovery or of preventing its loss quite frequently will be favorable. For example, the refinery skimming-pond losses referred to previously will be turned into a profit in the near future when the ponds are replaced by a closed gas-cycling oil-water separation flotation cell from which no vapors will escape.

What Must Be Known

The initial impetus to establish a vapor-loss prevention or recovery program of any type must come from an informed management. Just how much information

can you give your management about the situation in your plant so that it may evaluate the economic or political incentive in the situation and thus create a basis for decisions?

How much vapor is lost from this operation—or from that one—and what is its composition? What is the concentration of hydrocarbon vapors in the air around your plant—in the air over your city? How did you determine it—and is your method of analysis any good? Is the Haagen-Smit theory of smog formation valid and, if so, should it be extended in scope? For example, are there hydrocarbons other than the low-boiling olefins which should be investigated? What about acetylene? The 2,000,000 automobiles burning about 12,000 tons of gasoline per day in the Los Angeles area put out more than 200 tons per day of acetylene. What are the reaction products of acetylene and ozone? Do they damage crops or reduce visibility? Is ozone formed from nitrogen oxides by reaction with sunlight and, if so, how much nitrogen oxides does this furnace—or that one—or 2,000,000 automobiles—make, and what can be done to prevent its reaching the atmosphere?

The Policeman Is Here

These are only sample questions from a much larger number which could be asked. But they represent questions to which you should have better answers than the policeman—and soon. For if you still don't believe he is coming, just listen to this. I quote from the monthly report, dated July 17, 1951, of the director of the Los Angeles Air Pollution Control District, made at the end of the district's fiscal year, to the Los Angeles County Board of Supervisors, which reads in part as follows: ". . . unsaturated hydrocarbons are the major uncontrolled source of smog in Los Angeles County. . . . Current investigations will determine how much of the unsaturated hydrocarbons are entering the atmosphere in the areas where they are produced and how they react in the air to form their portion of the smog. This program will indicate how these important contaminants can be controlled."

Now those are pretty positive statements; and, coming from the head of a political agency, it would seem that they will have to be followed up by a pretty positive statement of results attained by this past year's program in order to obtain sufficient funds from the County Board of Supervisors for another year of expanding operations. The present fiscal year of the district will end within a few weeks' time. You may be certain that a report around that time will indicate the presence of a fairly large concentration of hydrocarbons in the Los Angeles atmosphere. And, if the past approach to the problem is not abandoned in favor of a more realistic one which correctly evaluates the contribution of automotive exhausts to hydrocarbon pollution of the atmosphere, well . . . don't look now, but that shadow you see is not from a smoking stack. It is the shadow of the policeman who already has his hand on the shoulder of the petroleum industry in Los Angeles County.

DISCUSSION

Chairman Vesper: Your paper points up a number of things, and indicates many problems which certainly deserve active and intensive investigation leading to an early and better understanding. I am sure it makes plain to many who have not had an adequate opportunity to go over it the implications and bases of the Haagen-Smit theory, and it also points up the political implications resulting from premature or perhaps inadequate understanding of some of these investigations.

D. L. Cleveland (Shell Oil Company, Wilmington, Calif.): I'm sure you will all agree that Mr. Jenkins has presented some very interesting food for thought. He has pointed out quite clearly that the origin of the so-called Los Angeles smog may not be so simple as some investigators would have us believe. I, too, have noticed that ozone-nhexene synthetic smog aerosols did not irritate my eyes or the eyes of those who were with me during the experiments. I should like to augment Mr. Jenkins's calculations with some I have made, based on the data released two weeks ago by the Los Angeles County Air Pollution Control District. You can draw your own conclusions:

1. Total hydrocarbon evaporation losses from processing and handling operations within the Los Angeles refineries are 7,000 bbl per day, 1.3 per cent of the crude intake.
2. The unsaturated C₄-C₆ hydrocarbons included in this total would result in a concentration of only 0.01 ppm in clear weather, or 0.08 ppm during an average intense inversion. Fumigation experiments were performed at approximately 4 ppm.

However, regardless of what we say here or discover in laboratory investigations, the policeman is coming. In the 45-page technical report just issued by the control district a total of approximately 12 pages is devoted to hydrocarbons. The control authorities have just requested specific information as to how and when all hydrocarbon emissions are to be stopped—regardless of whether they are saturated or unsaturated, large or small.

I have one more comment which I should like to make on Mr. Jenkins's paper. I realize that he was using evaporation losses from waste-water skimming ponds as an example of how corrective measures might eventually pay for themselves, but I should like to point out to those of you who are not familiar with refinery waste-disposal operations that the condition of which he spoke is not general throughout the industry. The standard practice is to use separators of API or modified API design, where continuous or semi-continuous removal of most of the hydrocarbons is accomplished without extensive evaporative surfaces. His findings, however, should stir us into looking critically into all of our operations to see whether loss-prevention equipment can be made to pay out either financially or with improved public relations.

Last week Dr. Haagen-Smit presented a new theory on ozone formation. He proposes that NO₂ reacts not only with olefins, but also with alcohols, aldehydes, and

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saturated branch-chain hydrocarbons. As this places more pressure on the petroleum industry, I should like to ask Mr. Jenkins if he can explain this latest theory.

Mr. Jenkins: I have talked with Dr. Haagen-Smit, and have read copies of the talks he made before the California petroleum industry. He has not mentioned any reactions for the saturated hydrocarbons and nitrogen dioxide in sunlight, which he now claims are responsible for the formation of ozone. Particularly, he points out that the unsaturated hydrocarbons are supposed to react with the NO_2 to give ozone which, in turn, reacts with the olefin to give the smog and to set up a chain where the ozone is formed. No reactions have been published. This merely points up that we are blamed on all sides instead of one, and we had better get busy and do something about it.

W. G. Green (General Petroleum Corporation, Los Angeles, Calif.): The paper by Mr. Jenkins covers quite adequately the situation as it now exists in the Los Angeles area, and it is certain that considerable confusion over causes and cures exists. However, the pollution problem is with us, and the most important fact to be considered is what do we in industry know about our own emissions. At present, in the Los Angeles area, industry is regulated on the amount of smoke, sulfur dioxide, and dust which can be liberated to the atmosphere. However, who can say what other emissions will come under regulation, and how soon. Currently much is being said about hydrocarbons and oxides of nitrogen. It would seem that our efforts should be pointed toward developing knowledge of what is coming out of our plants. As to the mechanics of conducting such surveys and methods of sampling and analysis, the Committee on Disposal of Refinery Wastes will soon have ready for distribution a series of manuals covering these various aspects.

Mr. Jenkins has pointed out the possibility of monetary realization from pollution control. This, I believe, is worthy of serious study on the part of those charged with pollution control and conservation activities. As examples, I would point to hydrocarbon losses from storage tanks and from skimming ponds, as well as byproduct sales, either by direct recovery or manufacture from waste materials. Data of this kind are needed for efficient operations, whether the policeman is coming or not.

In conclusion, I would again emphasize the absolute need for adequate data on effluent streams and on the atmosphere surrounding our plants. Only through this type of approach can we expect to develop a logical and sound answer to the ever-increasing pressure on pollution problems. It should also be pointed out that considerable effort is needed to promote realization on the part of regulatory bodies that the concentration in the atmosphere, or atmospheric load, is the important consideration. In other words, too much emphasis is being placed on total emissions at specific sources, and concentrations thereof, regardless of geographical location and climatic conditions involved.

J. H. Easthagen (California Research Corporation, Richmond, Calif.): I just want to point out what might happen under the procedures outlined in the early part of Mr. Jenkins's paper, "The Policeman Is Coming!"

After the policeman comes and pays you a visit, as he leaves he will probably hand you a list of particulars as to what he wants you to do to correct the situation at your plant. You cannot ignore this, nor can you protest too loudly. If you do, he will return—this time with an invitation for a public hearing.

The policeman dearly loves a public hearing. To him, it is a Roman holiday. At this public hearing you will find that it is almost like a family party. You will find that the prosecutor looks like the policeman; the judge looks like a prosecutor; the jury looks like the judge; and the executioner looks like the jury. The purpose of this public hearing is to get you to admit your sins against the public welfare.

Now it is very difficult to make a public admission and retire with honor. However, it can be done—which reminds me of a little story.

Mr. Jones was paid a visit by his minister, because Mr. Jones was an affluent person and the minister thought he could contribute to the church fund. Mr. Jones was not a black sheep, but he loved a little joke. (We might call him a gray sheep—he was probably exposed to too much smog.) So he told the minister that he would contribute to the fund if the minister made a public acknowledgment of the gift. Now Mr. Jones knew that the minister liked a little bit of after-dinner liqueur; so he sent the minister a gift which consisted of a check for the church fund, wrapped around a bottle of fine cherry brandy.

The minister needed the check for his church fund; so he decided he would make public acknowledgment of the gift in its entirety. Accordingly, next Sunday, at the conclusion of his sermon, he said that he wished to acknowledge the gift of a very substantial check from Mr. Jones—also some fruit, and the spirit in which it was sent.

Joseph C. Anderson (Union Oil Company of California, Rodeo, Calif.): I feel a certain reticence in facing a group of this caliber; but, in listening to the discussion of these papers, the thought came to me that I may be able to contribute something of value.

The first point I should like to make, based on past experience, is that the petroleum industry should—through its established agencies and individual facilities—continue its research work on the problem of smog. Nowhere is there a group of trained men better qualified to search and analyze this thing we now know to be a complex and complicated problem than can be found on the engineering staffs of the individual companies and the supported research staffs. Accomplishment will not be easy. Theories which have been proved wrong, false starts, and dead-end leads are things which plague research efforts, and must be overcome in solving the problem.

The best defense the industry has against unnecessarily corrective measures and an out-of-proportion

control effort is a heavy backlog of definitive information. When the policeman comes, he will be pointing not only his finger, but the public finger as well. It is hard to beat the public finger; because, while he is pointing it at you, "Mr. Public" is looking, and he is thinking. I am certain that without industry-sponsored research the work of your public-relations officers, your engineering staffs, and your budget planners is going to be much more difficult.

Sulfur dioxide has always been a prime target for air-pollution research. I have faced sulfur-dioxide studies until I was weary of the subject. I have been the research engineer—also the policeman—in an area where the one problem was to get rid of enough *dense black smoke* so that we could see what was going on.

The beginning of my interest in air-pollution problems came years ago while I was attending a university in a city where the primary fuel was bituminous coal. Driving the streets as late as 11 o'clock in the morning, it was necessary to turn my headlights on to see where I was going and avoid collision with other cars. That was smoke 2,000 ft to 3,000 ft in depth, and dense with free-carbon particles. The incidence of eye and nose irritation was comparatively low, although fastidious nostrils could detect with no difficulty the odor of coal smoke. In that city the control measures followed a normal pattern, viz., attacking first the black-smoke producers. Now that city has a smog problem and—although this is not admitted—a rising level of eye and nose irritation caused by finely divided "hot" hydrocarbon particles which react with moisture and other impurities to form the now familiar smog pattern. This is in a mountain-ringed valley, accompanied by an inversion trap. One conclusion is obvious. Vast amounts of free carbon seem to have a purifying effect—masking or preventing the formation of the irritating compounds. A semi-humorous lecture for the layman, entitled "Trading the Black Ring on Your Shirt Collar for Red Rings around Your Eyes," deals with this subject.

The smog of the West Coast cities is the "old-age" stage of the so-called normal smoke-control cycle, and we call it "air-pollution control." In cities coming out of the smoke into the smog, the saying is popular that "the people are more irritated by what they can't see than by what they can see." This does not mean that the smog is not visible; for it is. But its color, black-out power, and visibility characteristics are vastly different from those of the old-fashioned smoke cloud.

Heartening, indeed, is the fact that research workers assembled here recognize the complexity of the air-pollution problem, and are cognizant of the multiple contributing sources.

To my friends in the San Francisco Bay area, I should like to urge caution—not to poke fun at Los Angeles, because we also have a smog problem. It is here—around and on top of us—with all the trimmings of—surrounding mountains, inversion pattern, and the accumulative phenomenon accompanying it. The eye and nose irritation is not openly admitted; but, again, its incidence is apparent. Strangely, too, press releases from authoritative sources deny that the problem exists here.

Many of you gathered here probably saw our smog cloud this morning. Coming in from Berkeley and points north, the light was just right to make it show prominently. It was a very pronounced cloud, and anyone who has doubts about its true nature should try some color photography under it. Essential light rays are filtered out; color balance is upset; and we hear the common complaint about brownish-red and iridescent colors.

Who is responsible for the smog? The papers presented here have given a hint as to the scope of the problem. That *everybody* is in some way a contributor will draw no argument from me. Looking at ourselves, it has been shown that the basic elements of our operations are the production, refining, transportation, and marketing of oil and oil products. Some is lost all along the line. Balance these losses against the total input, viz., that used for fuel—the total products sold—and the picture begins to take shape. Thousands of consumers use petroleum and other products for fuel, lubrication, and industrial processes—and all of this lies beyond the control of the petroleum refining industry.

Let us be prepared for the policeman when he comes; do what is possible within sensible limits; but we should be able to show, depending on the area involved, that a total cleanup of the petroleum industry would involve less than a 5- to 10-per-cent improvement in the overall condition.

Chairman Vesper: I believe the two papers just presented—more particularly Mr. Jenkins's paper—certainly point up the fact that we should no longer view with alarm; but that, as refiners, we should give this matter some very concrete and definite action. I hope all those concerned will take that to heart and take it back home with them.

We turn now to a somewhat different aspect of the atmospheric pollution problem. In fact, in this instance, it is going to be broadened a little to include not only atmospheric pollution, but some phases of public pollution as well, as illustrated by the problem of an integrated refining operation closely within an urban area.

This report presents the experiences of cooperating with authorities to provide a picture of the progressive problem of disposal with increases in refinery capacity. The burning of high-sulfur vapors, the disposal of finished-gasoline vapors, the treatment of water, and the flue-gas neutralization problem of smoke abatement is treated.

INTRODUCTION

This paper, written with the ultimate in making a constructive criticism of the *Disposal of Refinery Wastes*,^{1, 2, 3a} is the geographical position of the Company's refinery in Detroit, Michigan, a relatively congested residential area within city limits, in a situation of full compliance with the municipal ordinances.^{8, 10, 18} Further, the maintenance of a minimum of proposals to avoid neighborhood complaints to avoid irreparable harm to public health.

This point is strikingly illustrated of some 10 years ago. An early "know-how" were responsible for uncontrolled atmospheric pollution, forced by our neighbors was brought forcefully to our attention. The situation permitted a success, however, we were subsequently successful in reconciling our lost friends. A parent success in this direct, unenviable position of exposure to disposal. Herein we present our recommendations.

Industrial Background

In the short time it has grown from a few barrels of refining capacity to a greatly expanded production spirit—higher, perhaps, the industry—has engendered processes, often in large quantities. Our company has

* Aurora Gas
† Presented by
* Figures refer