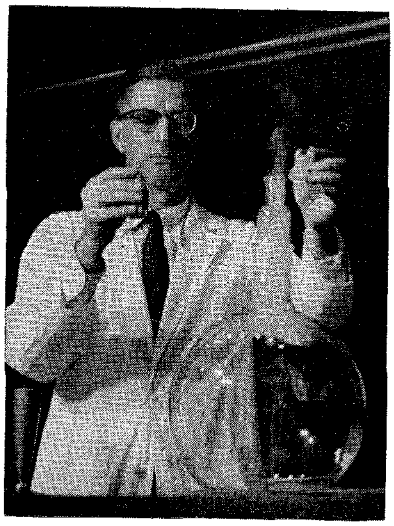
THE CONTROL OF AIR POLLUTION IN LOS ANGELES



by A. J. HAAGEN-SMIT

THE SAME METEOROLOGICAL and geographical conditions which made the Los Angeles basin famous set the stage for a serious air pollution problem when five million people and their industries began to crowd this area. The inversion condition, a warm layer of air above the colder, ground layer, prevents dispersal of the pollutants. This layer of polluted air is blown inland by a slow sea breeze during the day, to return frequently at night, carried by an even slower land wind.

Detailed meteorological studies at ground level show that on days of severe smog stagnant air conditions usually prevail during the night and early morning hours, which permit the build-up of pollution. When the inversion height is lower than 1,000 feet, air pollution becomes noticeable; people begin to complain of eye irritation and odor, farmers notice damage to their crops, and a dense haze blankets the area.

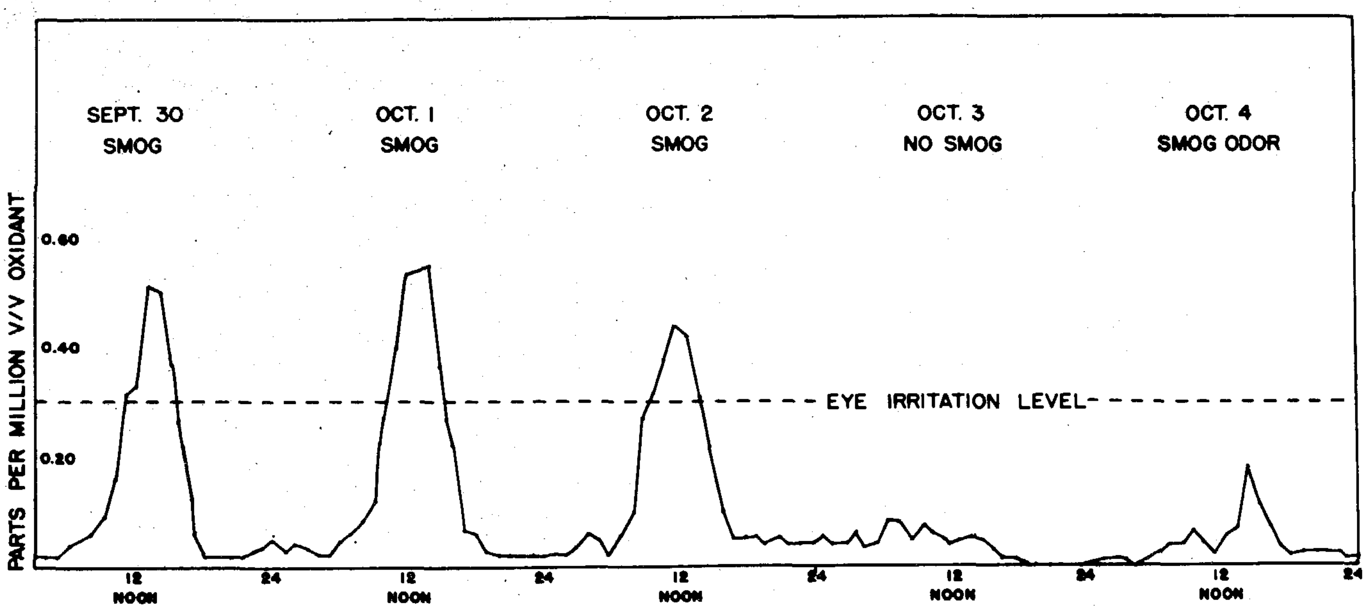
The chemical analysis of smog air shows the presence of a great number of materials, among which are sulfur dioxide and dusts, well known as trouble-makers in other industrial areas. Control measures by the Los Angeles County Air Pollution Control District have brought these emissions below the 1940 level, when the word "smog" was still unknown in California. Hundreds of tons of sulfur are now recovered at the refineries, and emissions of metal dusts from foundries and steel mills are largely controlled.

Public burning dumps have been abolished, but private rubbish burning still goes on, and there is considerable opposition to replacing it with more advanced disposal systems. Another needless source of pollution is created by the "smokers"—automobiles which, because of poor maintenance, continually emit smoke from their exhausts. But even cars in good condition produce smokes which, by depositing on the outside as well as on the inside of our houses, raise our maintenance costs. These same deposits are at present causing concern to the medical authorities.

While these visible sources are not responsible for typical smog damage to crops, and the eye irritation caused by them is mostly of a local nature, their contribution to at least one aspect of the smog—the haze—already justifies the insistence of the Air Pollution Control District that the numerous small sources of smokes and fumes should be controlled. Anyone desiring clean air should support the authorities in this part of their difficult and often unpopular task, which is essential to obtaining better visibility.

This part of the control program is not expected to reduce considerably the eye irritation felt over hundreds of square miles, nor will it give relief to the farmer, reduce the peculiar chemical odor associated with smog, or prevent excessive rubber cracking in this area.

Chemically, the most characteristic aspect of smog is its strong oxidizing action. The intensity of this oxidizing action correlates closely with eye irritation and other smog symptoms such as plant damage, rubber cracking, and smog odor. The amount of oxidant can readily be determined through a quantitative measurement of iodine liberated from potassium iodide solution, or of the red color formed in the oxidation of phenolphthalin to the well-known acid-base indicator, phenolphthalein. To demonstrate these effects, it is only necessary to bubble a few liters of smog air through the



Chemically, the most characteristic aspect of smog is its oxiding action. Daily determinations show that the oxidant rises shortly after sunrise, reaches a maximum in Pasadena between 1-2 p.m., is practically absent at night.

colorless solutions. A marked color change occurs, indicating the presence of oxidizing materials.

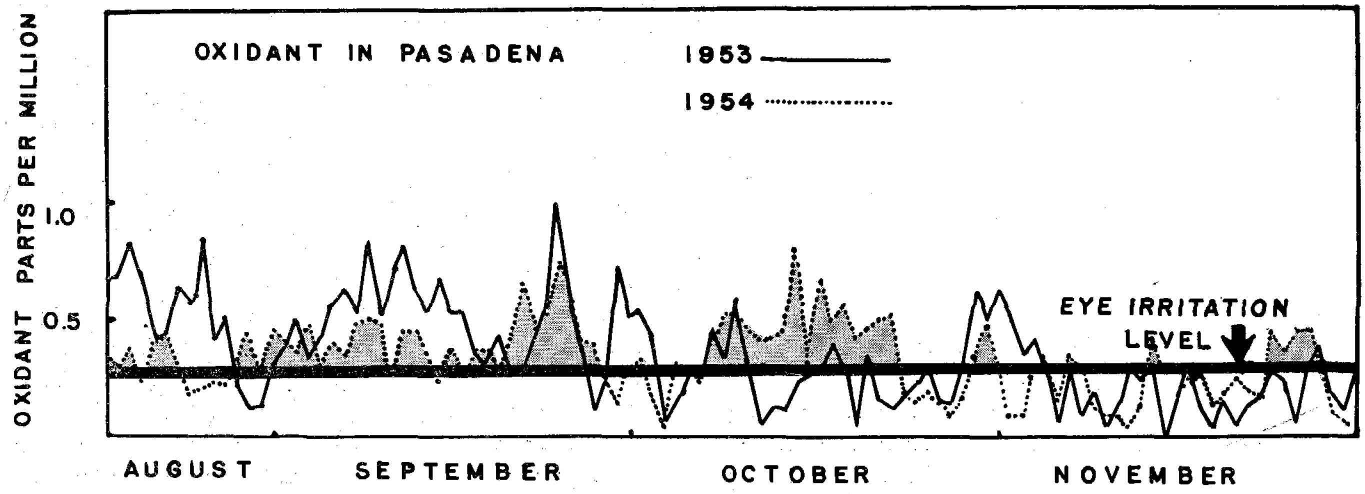
Daily determinations (as in the chart above) have shown that shortly after sunrise the oxidant rises, and reaches a maximum at some time during the day—in Pasadena most often from one to two o'clock. At about sundown the oxidant decreases considerably, and it is practically absent during the night. We have been measuring these effects for more than a year, and have found that when the oxidant value passes a certain level, eye irritation occurs.

The chart below shows the fluctuation in the daily maximum recorded at the California Institute of Technology in Pasadena. The fluctuations are largely caused by meteorological conditions. However, there is a distinct weekly pattern which shows that Sundays are definitely less smoggy than other days of the week, especially Thursdays and Fridays. This phenomenon is not clearly understood. It could be due to reduced activity of industry as well as to a change in the traffic pattern during week-ends.

The value of these records lies in the objective estimation of smog intensity, and when continued, the data will be an aid in judging progress made in smog control.

From these records we can see that the worst smog period this year, from August through October, was not as bad as last year, either in intensity or in duration (hours per day). Nevertheless, the eye irritation level was exceeded in Pasadena during that time on 65 out of 90 days.

The oxidizing action of smog air is due to the release of large quantities of organic material, mostly hydrocarbons, and oxides of nitrogen. When these gases are exposed to sunlight, eye-irritating substances are formed, and in the fumigation of plants typical smog damage *symptoms are produced. At the same time aerosols*



Fluctuations in daily maximum of oxidant in Pasadena show that this year's worst smog period was not as bad as last year's—and reveal a distinct weekly pattern, with Sundays definitely less smoggy than other days of the week.

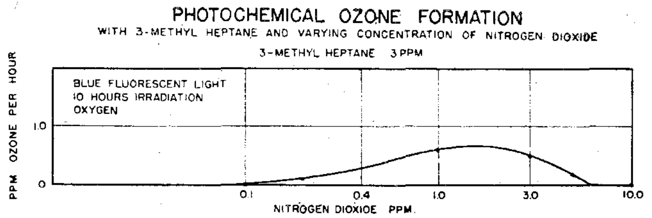
(pollutants in the air which are so small they do not settle out, but are in stable suspension) are formed and a smog odor is apparent. Plant damage observed in this area is quite different from that caused by sulfur dioxide or fluorine compounds, and its reproduction in fumigations with the photochemical oxidation products of gasoline and nitrogen dioxide (NO_2) was the basis of one of the most convincing arguments for the control of hydrocarbons by the oil industry.

It was interesting that the same damage could be obtained when ozone was mixed with gasoline vapors in the absence of sunlight. In the vapor phase reaction of ozone with olefins present in gasoline we may expect the formation of ozonides and other substances of peroxidic nature, as well as acids and aldehydes. The possibility of producing typical plant damage and other smog symptoms by the oxidation of hydrocarbons either with nitrogen dioxide, air and sunlight, or with ozone, indicated that similar products are involved, and further research has established that *ozone actually is produced in the air by the action of sunlight on organic material in the presence of nitrogen dioxide.*

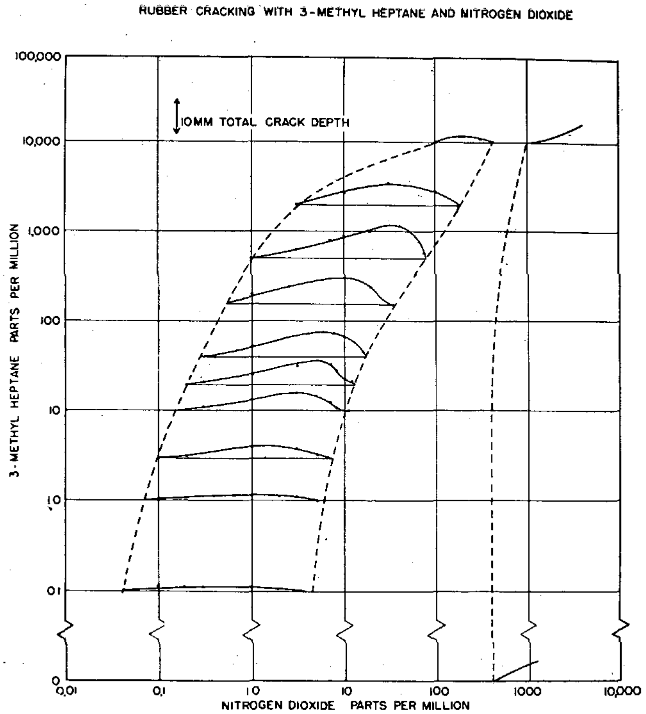
The concentrations of organic materials—hydrocarbons, aldehydes and acids—and those of the oxides of nitrogen determined in our polluted air fully account for the high concentrations of ozone found in this area. During severe smog attacks, ozone concentrations of 0.5 ppm., twenty times higher than in country air, have been measured. From such analyses the quantity of ozone present in the basin at that time is calculated to be about 500 tons.

Since ozone is subject to a continuous destruction in competition with its formation, we can estimate that several thousand tons of ozone are formed during a smog day. It is obvious that industrial sources or occasional electrical discharges do not release such tremendous quantities of ozone. A transport of ozone from the upper air is also out of the question during inversion conditions.

The mystery of the abnormally high ozone content of smog air was solved several years ago, and our discovery that photochemical oxidation of organic material is accompanied by ozone formation gave further scientific evidence for the necessity of controlling hydrocarbon emissions. It also made clear why the oxidant values rise during the day and decrease as soon as the day is over. Ozone, a major part of the oxidant, is generated in the presence of sunlight, but as soon as this production decreases in the evening, the reactions which destroy ozone gain the upper hand and rapidly remove it from the atmosphere. The eye-irritating reaction products, however, can often be noticed in the air for a much longer time.



Photochemical formation of ozone is responsible for severe rubber cracking in this area. Cracking of standardized rubber is now a test method for estimation of ozone in air.

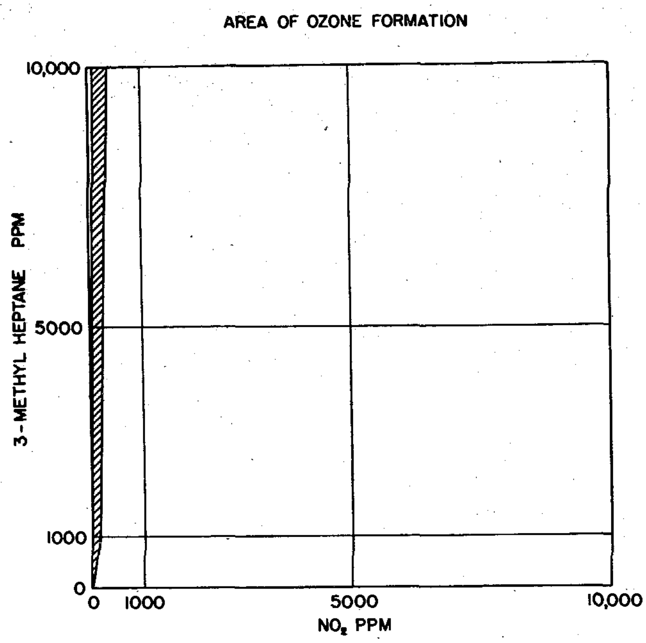


Phenomenon of ozone formation is limited to a definite range of concentration of hydrocarbon and nitrogen dioxide.

The photochemical formation of ozone is also responsible for the severe rubber cracking observed in this area. Rubber is an unsaturated hydrocarbon, and its reaction with ozone is similar in principle to that of ozone and the unsaturated components present in gasoline. We have used the cracking of standardized rubber as a convenient and highly specific test method for the estimation of ozone in the air. During severe smog initial cracking appears in about four minutes, as compared to an hour or more required on smog-free days, or at night.

In duplicating the photochemical ozone formation in the laboratory, known concentrations of hydrocarbons and nitrogen dioxide were exposed to artificial light and the ozone formed was measured by the rubber cracking method or by chemical means. It is found that for a given hydrocarbon concentration—for example, three parts per million—a small but definite amount of nitrogen dioxide is necessary before ozone can be detected. After passing through a maximum at about 2 ppm, of NO_2, the ozone formation decreases, and is nearly absent at about 5 ppm., as shown in the chart at left for 3-methylheptane.

The results of many measurements at different concentrations of hydrocarbon are presented in the chart at the above on a logarithmic scale. We see that the phenomenon of ozone formation is limited to a definite range of con-



Limited area of concentration in which ozone formation occurs is clearly shown in linear presentation.

centration of hydrocarbon and nitrogen dioxide, and this is even more striking when a linear presentation is used (above). The composition of the air in Los Angeles during smog days is in the order of 0.4 to 0.8 ppm. of NO_2 and 1-2 ppm. of hydrocarbon, and falls directly within the range at which ozone formation occurs. The amounts of ozone formed in laboratory experiments correspond closely to those measured outside.

The phenomenon that ozone formation is limited to definite relative proportions of hydrocarbon and nitrogen dioxide, observed with 3-methylheptane, is apparently quite true for other saturated hydrocarbons, as well as for olefins, and their oxidation products, acids and aldehydes. It has been observed that as the length of the carbon chain increases from four to nine carbon atoms, the ozone-forming capacity becomes greater. Methane, ethane and propane were found to be inactive. The highly branched hydrocarbon, 2, 2, 3-trimethylbutane (triptane), well known for its anti-knock value and high critical compression ratio, does not form ozone in any appreciable quantities, even upon prolonged irradiation. On the other hand, the unsaturated n-heptene-3 is very active in this respect. The chart at the right compares the relative ozone-forming capacity of these compounds with our standard hydrocarbon, 3-methylheptane. This marked effect of branching and the location of double bonds on ozone formation is being further investigated to explore the possibility of a change in fuel composition.

From a practical point of view, it is important that the irradiation of gasoline vapors (straight run, as well as cracked) in the presence of nitrogen dioxide also leads to the formation of ozone, and the Los Angeles County Air Pollution Control District has demonstrated the ozone-forming property of air near sources of hydrocarbon release.

The oxides of nitrogen necessary for this reaction are formed in all high temperature combustions through a reaction between nitrogen and oxygen from the air. The main sources are the burning of fuel gas, fuel oil and gasoline, whereby nearly 500 tons of nitrogen oxides are produced per day. No satisfactory way for the control of nitrogen oxides is known yet, and therefore most of the attention is given to the other partner in the smog reaction, the hydrocarbons.

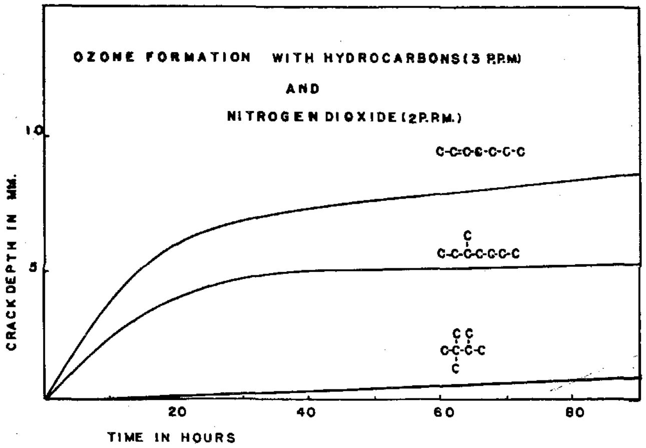
The hydrocarbons are emitted to the air by evaporation from storage tanks and through many activities of the oil industry. The control of these sources is well under way, and about 400 tons of hydrocarbons per day are now being collected which formerly went to waste. The remaining emissions are estimated to be approximately 250 tons per day.

Automobile exhaust

The other large source of hydrocarbons is automobile exhaust. The exhaust contains both ingredients for the production of smog—hydrocarbons and oxides of nitrogen—and this ready-made mixture gives all of the typical smog symptoms upon irradiation with sunlight.

The exact knowledge of the range of concentration of hydrocarbon and NO_2 where ozone formation takes place was very helpful in showing that automobile exhaust after irradiation gives ozone. The only data required are the hydrocarbon and nitrogen dioxide concentrations in the exhaust sample. Then from the graph on page 15 we can read how far the sample must be diluted to reach the ozone-forming area.

The exhaust of a cruising car contains about 600 ppm. of NO_2 and 600 ppm. of hydrocarbon. A dilution of 600 to 1 brings it into the area of ozone formation. For acceleration exhaust, with its high NO_2 content, a dilution of 1,000 to 1 is necessary. Deceleration exhaust falls within the area, and idling exhaust contains too little NO_2 to be able to form ozone upon dilution. However, if we mix deceleration, idling and acceleration exhausts, the "stop-and-go" phase of driving, we have a mixture that is equal to that of cruising exhaust, and ozone can be formed.



Comparison of relative ozone-forming capacity of other saturated hydrocarbons with standard, 3-methylheptane.

The important conclusion is that somewhere behind the car the exhaust gases will be sufficiently diluted to form ozone.

More than 4,000,000 gallons or 12,000 tons, of gasoline are consumed each day in the Los Angeles area. To this should be added 30,000 gallons of lubricating oil which are also burned or lost. The loss in unburned or partially burned gasoline from the exhaust is about seven to ten percent of the gasoline used, and it is estimated that the emission of hydrocarbons to the air is on the order of 300,000 to 400,000 gallons, or about 1,000 tons per day.

Driving conditions in Los Angeles

The Los Angeles County Air Pollution Control District has determined the gasoline losses during idling, acceleration, cruising and deceleration. The losses are not equally divided over the different phases of automobile operation. As a result of a survey on driving conditions in Los Angeles, we can estimate the time spent on each phase. Tabulation of these results shows the relative importance of the different phases of automobile operation with respect to hydrocarbon emission.

DRIVING CONDITION	IDLING	ACCEL.	CRUISING	DECEL.
Time Driven—%	18	18	46	18
Gasoline—gal. hr.	0.45	2.25	1.52	1.22
Hydrocarbon Concen. mg./liter	5.8	0.8	0.9	15.0
Exhaust Flow cu. ft./min.	14.2	56.0	28.4	30.2
Hydrocarbons into Atmosphere—units	17	8	13	62

It is interesting to note that although only 18 percent of the driving time is spent in deceleration, 62 percent of the total hydrocarbon loss occurs during that time. Stop-and-go traffic, which includes deceleration, idling and acceleration, contributes 87 percent to the total loss. Substantial improvements in exhaust emission can therefore be expected from a reduction in the number of required stops. The use of freeways allows a constant flow of a large number of vehicles with a minimum of stop-and-go driving. The construction of freeways is therefore an excellent means towards the reduction of exhaust fumes.

The automobile industry in Detroit is seeking a solution through improvements in engine design, carburetion, etc., and it was recently announced that a 30-50 percent reduction of the hydrocarbon emission would be feasible.

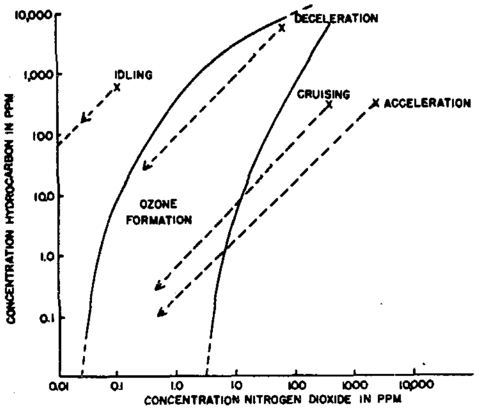
The increase in the number of freeways and the improvements in fuel economy are, of course, most welcome to the driver. This cannot be said for the attempts to reduce the exhaust emission through the use of rather expensive corrective devices on the exhaust. There is a great deal of misconception about the purpose of these gadgets and the conditions under which they have to operate. The removal of carbon monoxide, for example, does not help in the reduction of smog. It is often overlooked for each gallon of fuel consumed, one quart of water and more than half a pound of chemicals are leaving the exhaust. Removal by scrubbers or chemical agents is therefore impractical.

The main ingredients that we want to remove from the exhaust by such devices are of hydrocarbon nature, and the only practical way to remove them is by combustion. At the present time, two so-called "afterburners" show definite promise. However, considerable time for testing is needed before these muffler-type burners can be recommended for adoption by the two-and-a-half million automobile owners in this area. It is held possible that these mufflers can be installed in the not too distant future on trucks and buses.

Also under way are investigations on the effect of fuel composition on the irritating properties of the exhaust gases. The feasibility of converting at least buses and trucks to the use of LPG (Liquid Petroleum Gas) is being considered, since hydrocarbons such as propane and butane are free from some of the objectionable qualities of gasoline. Our findings that there is a considerable difference in the ozone-forming capacity of different hydrocarbons suggest that investigation of the behavior of individual hydrocarbons might give a lead towards improvement in fuel composition. We should not forget, however, that the high temperatures which occur during the explosion change these compounds, and that the evaluation of their smog-forming character should be made not only on the fuel itself, but also on the products resulting from its incomplete combustion.

While engineering is in progress on the exhaust problem, everyone can help in the reduction of exhaust emissions by keeping his engine in good mechanical condition, by practicing the driving habits recommended when gasoline was rationed, by supporting the construction of freeways and by urging a greatly improved public transportation system.

PHOTOCHEMICAL OZONE FORMATION FROM AUTOMOBILE EXHAUST



Graph shows how far a sample of auto exhaust must be diluted to reach area where ozone-formation takes place.

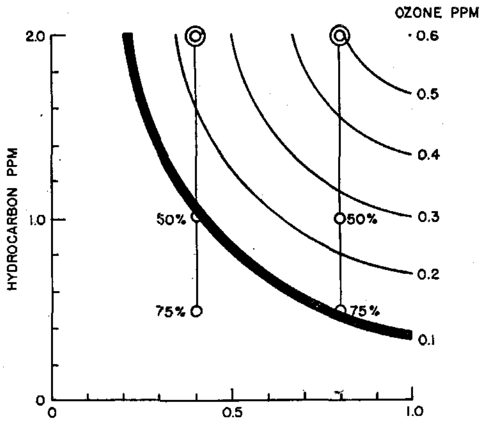
In order to evaluate the result of such reduction, we have to refer to our graph showing the ozone formation at different concentrations of hydrocarbon and NO_2. A more detailed view of the region of concentration measured during the smog is shown below. This graph shows the ozone level reached after four hours' irradiation with sunlight at varying concentrations of nitrogen dioxide and 3-methylheptane. Notwithstanding the use of a single hydrocarbon in these experiments, the values of ozone found seem to agree well with those found during smog periods, when not only the concentration of hydrocarbons, but also the concentrations of their oxidation products are used in the computation. This method of computation is necessary because the concentrations of hydrocarbon and NO_2 determined during a smog attack do not represent the initial concentrations. Oxidation is continuously going on, reducing the original hydrocarbon and NO_2 concentrations and increasing the concentrations of aldehydes, acids and other oxidation products.

Ozone formation

In the first place, we notice on our graph that the concentration of ozone formed is directly proportional to the product of the hydrocarbon and NO_2 concentrations. An increase of 20 percent in the hydrocarbon and NO_2 will therefore result in a 44 percent increase in the ozone formation, and this might well explain some of the increase in ozone levels during the last five years.

The graph also allows us to predict the effect that will be obtained by a reduction in the hydrocarbon. If the initial concentration of hydrocarbon is in the order of 2 ppm., and that of the nitrogen oxides 0.4 ppm., a reduction of 50 percent in hydrocarbon will enable us to remain just below the threshold of irritation of 0.1 ppm. of ozone. However, when the NO_2 concentration is 0.8 ppm., a quantity which has actually been found during severe smog, a 75 percent reduction in hydrocarbon (from the original concentration of 2 ppm.) would be necessary to reach the same threshold. Unfortunately, the tendency at present is towards a steady increase in the NO_2 concentration, which demands greater and greater efficiency in hydrocarbon recovery. The alternative is to reduce the NO_2 concentration as well as that of the hydrocarbons.

OZONE FORMATION WITH 3-METHYL HEPTANE AND NO_2



Concentration of ozone formed is directly proportional to the product of hydrocarbon and NO_2 concentrations. Graph shows potential effect of hydrocarbon reduction.

The sources of smog are well known, and there is general agreement that the control measures taken towards the reduction of dusts, smoke, sulfur dioxide and hydrocarbons were fully justified, and that this program should be continued with vigor.

Vigilance and planning needed

There is every reason to expect that the present difficulty will be overcome. The question is, however, how long will this improvement last? Every reduction in the harmful emissions from the industrial plants is but a partial one, and a small percentage of the pollutants still escapes into the air. The reduction in the emissions from the automobiles through exhaust devices or improvements in engine performance will probably be, in practice, not much better than 75 percent. The oxides of nitrogen, partners in the smog-forming reactions, have continued to increase at a rate of four to five percent per year without any practical means of their control in sight. This unfortunate fact, together with a renewed, gradually-increasing emission of organic materials, will eventually result in even higher concentrations of the irritants, such as ozone, than we notice today. This toxic agent may then exceed the level which conservative hygienists consider unhealthful. If the present trend continues, we might expect in ten or twenty years a repetition of our unpleasant experiences of today. At that time, however, a further reduction will be considerably more difficult and expensive, and will have to include the control of oxides of nitrogen.

To insure clean air for the future, the present control measures will have to be implemented by bold civic planning which will include not only the city of Los Angeles, but the entire Los Angeles basin. Plenty of breathing space in the form of spacious parks should be included in the plans, together with the creation of a badly needed rapid public transportation system. City planners and engineers may even have to scrutinize carefully such revolutionary proposals as the relocation of industries and power stations, community air purification plants, and other similar projects which may seem fantastic at this time.

Fresh air limited

We have now received two warnings that our fresh air supply is limited. The first, a wave of eye irritation during the war years, was controlled within a year through corrective measures at a single plant. The second attack of severe air pollution has lasted eight years and involves hundreds of industries and millions of people. We shall overcome our immediate problem, but only constant vigilance and thorough planning will assure a permanent solution.