*Max Yavno photograph from The Los Angeles Book*

# THE AIR POLLUTION PROBLEM IN LOS ANGELES

by A. J. Haagen-Smit

AIR POLLUTION IS NOT a unique problem of our machine age. In about 1300 A.D. a royal decree by the King of England forbade the use of a certain type of coal because it produced vapors damaging to the health. A committee of investigation was set up to punish the infringers by fines and demolish their ovens in case of repetition. One unfortunate individual was condemned to death because he had infringed the smoke rules three times.

I felt greatly relieved when I read in a recent issue of the Pasadena *Star-News* that a kiln operator in Los Angeles had just received his 54th notice of violation of the anti-smog laws and was fined $1,000 and sentenced to five days in jail—a sentence which his lawyer promptly appealed. This comparison shows, among other things, that after 650 years air pollution is still with us. Some of the problems are very much the same as then, except
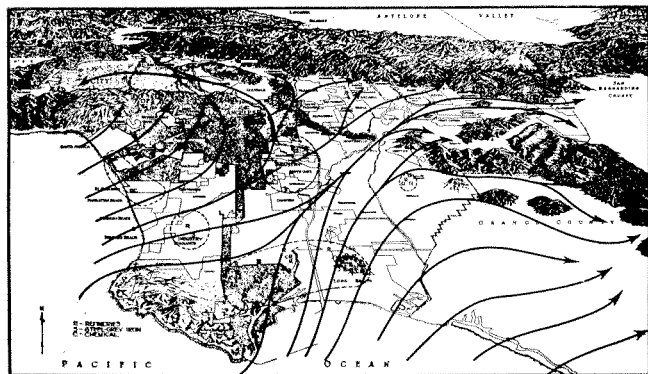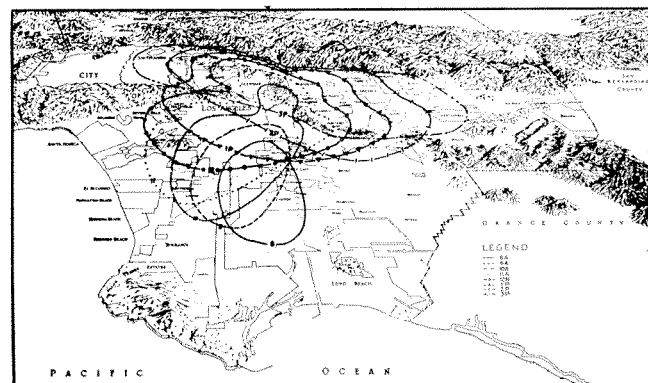
Wind direction in Los Angeles County
Summer—9 a.m. to Noon
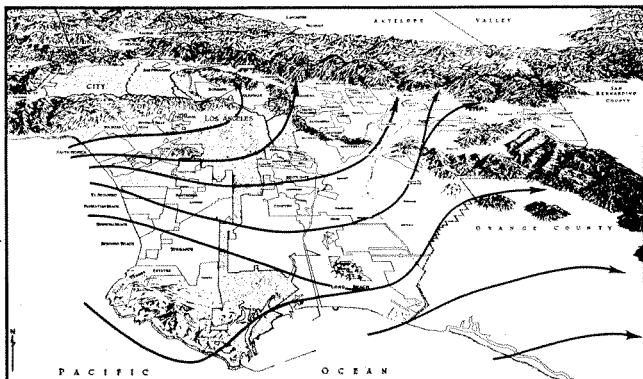
Wind direction in Los Angeles County
Summer—Noon to Midnight
Winter— Noon to 4 p.m.
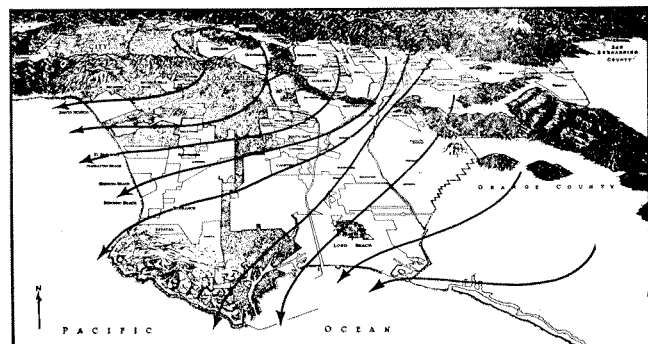
Wind direction in Los Angeles County
Summer—Midnight to 7 a.m.
Winter— 7 p.m. to 10 a.m.

Position of area of eye irritation at various times of day
in Los Angeles County—8 a.m. to 3 p.m.

Charts from Industrial and Engineering Chemistry, November '49

that the magnitude of the pollution is many times greater.

Usually we consider the air as an unlimited reservoir for our refuse. However, in densely populated areas we soon find out that this is not true, and at present we are sadly aware that there are limits to the amounts of material which we can send up into the air without creating a nuisance and even health hazards. This is especially true when geological and meteorological conditions favor the accumulation of air pollutants.

A favorable situation

Such a situation exists in the Los Angeles area, where a half-circle of mountains prevents the free movement of the air. Early in the morning a slow sea wind of a few miles per hour carries the exhausts of the great city up to the high mountain barrier in the north. In the evening the wind turns, and the pollutants move seaward. Usually the speed of this land breeze is too slow to be very effective in cleaning the area.

While the air is hampered in its free movement in a horizontal direction by the mountain barrier, meteorological conditions limit the movement in a vertical direction. Meteorologists have observed that during a large part of the year the lower layers of the air over the Los Angeles area have a lower temperature than the higher ones. The colder air, because of its higher density, is not able to rise, and it is just this layer that contains the gases, smokes and fumes released in this area.

This so-called temperature inversion is quite frequent, though the height of the layer is very different on different days, and may range from several hundred to several thousand feet. Complaints about smog are usually received when the base of the inversion layer is from 600 to 1200 feet.

A limited reservoir of air

Under these conditions the unlimited reservoir of air has shrunk considerably; however, it is still of enormous size. When we look at a map of this area on which has been plotted the movement of the cloud of eye irritants, we notice a gradual displacement and spreading towards the San Fernando Valley in the northwestern direction and towards San Bernardino in the eastern direction.

When such an area, of approximately 25 by 25 miles, is covered uniformly with a smog layer which we will assume to be about 1000 feet thick, we can calculate that approximately 500,000,000,000 cubic meters of air have been polluted. Since one cubic meter weighs about 1.3 kilograms, the actual weight of this smog-containing layer is about 650,000,000 tons. This enormous tonnage is often overlooked in "quick cures" for smog, when proposals are made to place fans on the mountains or drill tunnels through the mountains to drive away the smog.

Knowing the volume of air involved gives us a basis for a calculation of the quantities of materials which are polluting our atmosphere. If a substance gives irritation in a concentration of one part per million, we need in

this area 650 tons of material to show this effect. When only one tenth of a part per million is necessary for irritation, we need 65 tons; and for one hundredth of a part per million 6.5 tons must be released.

It is interesting to compare these values with a list of the threshold concentrations of some of the most potent war gases, all of which have threshold concentrations above one hundredth of a part per million. For one of the most potent tear gases, chloro-acetophenone, we need 150 tons to cover an area such as we are dealing with, to give eye irritation. For the war gases Lewisite and mustard gas, we need hundreds of tons to make life rather unpleasant. Further assurance that we are not in immediate danger comes from the column in the table below, showing the enormous tonnage which is necessary for lethal action.

WEIGHT IN TONS TO CAUSE IRRITATION IN 625 SQ. MILES INVERSION BASE 1000 FT. VOLUME OF AIR 500,000,000,000 M³ WEIGHT 650,000,000 TONS				
	SMELL	IRRITATION	TEARS	LETHAL IN 10 MIN.
ETHYL MERCAPTAN	0.02 (20 Kɢ)			
SYNTH. MUSK	0.005 (5 Kɢ)			
SKATOL	0.0002 (0.2 Kɢ)			
ACROLEIN		80	3,500	180,000
FORMALDEHYDE			400	
CHLORO ACETOPHENONE			150	400,000
CHLORINE		185		3,000,000
LEWISITE			400	60,000
SULFUR DIOXIDE			30,000	3,000,000

Our sense of smell usually responds to much smaller quantities of material than those necessary for irritation. One thousandth of a milligram of ethyl mercaptan (a relative of the skunk smell) released in a small auditorium can be readily detected by smell. If we extrapolate this example to the 25 by 25 mile area, we find that 20 kilograms (about 46 pounds) of ethyl mercaptan released at the City Hall in Los Angeles would be noticed in Pasadena. For a similar experiment with musk or skatol (one of the constituents of feces), the quantities necessary would be only about six pounds and a half a pound, respectively. These exceedingly low threshold values for odor perception are in accord with the common observation that the smell of smog is noticed long before there is any complaint of irritation.

Sources of pollution

We have seen that the quantities involved in irritation over such a large area run into hundreds of tons. These large quantities can be released by industries handling a large tonnage of material, or by numerous small offenders. At one end of the scale we find the petroleum industry, where a few refineries are handling many thousands of tons of material every day. But the half million automobiles driving around in Los Angeles contribute their share to air pollution, too. Together they burn approximately 12,000 tons of gasoline daily. Even if the combustion were 99 percent complete, which it certainly is not, 120 tons of unburned gasoline would be released. Another example of this type of pollution is the private incinerator, where the large number compensates for the small quantity released by the individual.

The analysis of air contaminants has some special features, due to the minute amounts present in a large volume of air. The state in which these pollutants are present—as gases, liquids and solid particles of greatly different sizes—presents additional difficulties. The small particles of less than one micron diameter do not settle out, but are in a stable suspension and form so-called aerosols.

Collecting air contaminants

The analytical chemist has devoted a great deal of effort to devising methods for the collection of this heterogeneous material. Most of these methods are based on the principle that the particles are given enough speed to collide with each other or with collecting surfaces. In the impactor, the air is drawn through a small slit, thus attaining a velocity close to that of sound. The particles in the air colliding with a glass slide are deposited on the slide and can be observed microscopically. A sample of Los Angeles' air shows numerous oily droplets of a size smaller than 0.5 micron, as well as crystalline deposits of metals and salts.

In a thermal precipitator the same principle is applied by passing the air over a heated wire which is placed between cooled surfaces. The particles move from the hot wire to the cooler surface, and are there deposited. Other instruments cause agglomeration of the smog particles by accelerating the particles with ultra sound waves, or through the application of a strong electric field. Many of these different techniques are used in industry to remove aerosols from waste material, and are known as Venturi scrubbers, sonic and electric precipitators.

Material collected from an electric precipitator was shown to consist of approximately one half inorganic material such as silica, traces of lead, zinc, copper, iron and a variety of other metals; their oxides; and salts such as sulfates, nitrates, nitrites and ammonium salts. The other half of the collected material consisted of organic material, which is partly soluble in fat solvents, and which contains hydrocarbons, aldehydes and organic acids. The insoluble organic material contains fibrous material, carbon and salts of organic acids.

Although the electric precipitator allows the processing of large quantities of air, a disadvantage of this method is the possibility that, under the influence of the corona discharge in a precipitator, secondary reactions would modify the organic materials. Therefore, the study of organic pollution has been conducted mainly on material collected on filters, or obtained from scrubbers. When air is passed through a filter paper, the paper takes on a grey appearance, and extraction with organic solvents gives an oily material. Subsequent extraction with water removes salts of organic, as well as inorganic acids.

However, this method too has disadvantages, since

most of the volatile material is lost. For this reason, extensive use has been made of traps held at very low temperature. Mass spectrographic studies on the collected dilute aqueous solutions have been useful in the analysis of the hydrocarbons present in the atmosphere.

For the isolation of special groups of substances, scrubber techniques are often useful. In our studies on the organic acids present in the air, scrubbers with sodium hydroxide were used. However, the most common organic acid in the air, carbon dioxide, occurs in quantities several hundred times greater than those of the air pollutants. It is therefore necessary to start with a large quantity of concentrated sodium hydroxide to be able to collect sizable quantities of the organic acids.

In our experiments we started with several liters of ten percent sodium hydroxide and, in a run of several days, made a very expensive sodium carbonate from 30,000 cu. ft. of air. However, after careful acidification and ether extraction, several tenths of a gram of organic acids could be extracted.

The identification of these acids can be made by converting them into derivatives which have characteristic melting points. Before this can be done, they must be separated from each other. Such separations, with small quantities involved, can be accomplished with chromatographic procedures. We have used a method whereby the acids are converted into the phenylphenacyl esters, which have the advantage of fluorescing in ultraviolet light.

Identifying acids in the air

When the mixture of derivatives is passed through a column of silica, a number of fluorescent bands appear, each representing a simple compound or a mixture of closely related acids. In this way we obtained fifteen of these bands, illustrating the complexity of the acid mixture present in the air. Some of these acids are normal and branched-chain ones; others contain, in addition to the carboxyl group, keto- and hydroxyl groups.

For a routine analysis of the air when no detailed separation of the collected material is intended, we rely on the specificity of the reagents. When, for example, a solution of sulfanilic acid and alpha naphthylamine turns pink when air is bubbled through, we are reasonably certain of the presence of nitric oxide.

The difficulty comes when we use less specific reactions or determine groups of substances on the basis of their oxidation, reduction power or acidity. For example, if we wish to determine the oxidizing material in the air, the amount of iodine liberated from potassium iodide solution can be used as a measure of this activity through titration with sodium thiosulfate or electrometric titration.

This total oxidizing capacity does not allow the making of any prediction as to the specific nature of the compounds present, and the results are further complicated by the possible presence of reducing substances which act in the opposite way. The iodine liberation is a balance of the two effects, and separate determinations for a number of compounds such as hydrogen peroxide, nitrogen oxide and reducing substances are necessary to enable us to explain this liberation quantitatively.

In the Los Angeles area it was found by several independent investigators that the liberation of iodine from potassium iodide was relatively high, and exceeded by several times the amount which could reasonably be expected as a result of the presence of ozone. With reagents more specific than potassium iodide, such as the dye, indigo-sulfonic acid, it is found that the ozone content cannot exceed a few parts per hundred million. But even these reagents are not fully specific, and scrubbing the air with a solution of ferric chloride and postassium ferric cyanide, which does not react with ozone, reduces the apparent ozone content still further. Semiquantitative experiments on rubber-cracking support these lower figures for the ozone content in this area.

High oxidizing powers of L.A. air

It is clear that the determination of the oxidizing compounds needs a great deal more study, and at the present time we are faced with the difficulty of finding an explanation for the high overall oxidizing power of the Los Angeles air. Since none of the inorganic pollutants gives an answer to this problem, it is only natural to look for the presence of organic material which may liberate iodine from potassium iodide solutions.

The organic substances in the air are of manifold origin and are subjected to sunlight, air and water; and as a result a rather complicated mixture can be expected. It is, therefore, of advantage to consider first what the sources of organic material are, and to what degree we can hope to analyze for these compounds.

The volatile material released into the air consists of hydrocarbons, saturated and unsaturated, originating from products derived from the petroleum industry and industries using solvents of different kinds. This includes all the material lost at the oil fields, refineries, filling stations, automobiles, etc.

Products of incomplete combustion

Then we have to consider the products of incomplete combustion from fuel as well as garbage of all kinds. In the literature we find detailed analyses for a few of these products. For a representative petroleum, the National Bureau of Standards published the identification of approximately 90 hydrocarbons. These are mostly saturated, whereas in the cracked gasoline extensively used nowadays there is a large amount of unsaturated hydrocarbons.

The products from the combustion of fuels have not been studied very thoroughly. Some of these products are carbon monoxide, methane, formaldehyde, acrolein and phenols. Similar unsatisfactory data are available on the combustion products of garbage. Its major components are of plant and animal origin, and it contains a high percentage of wood and paper. The
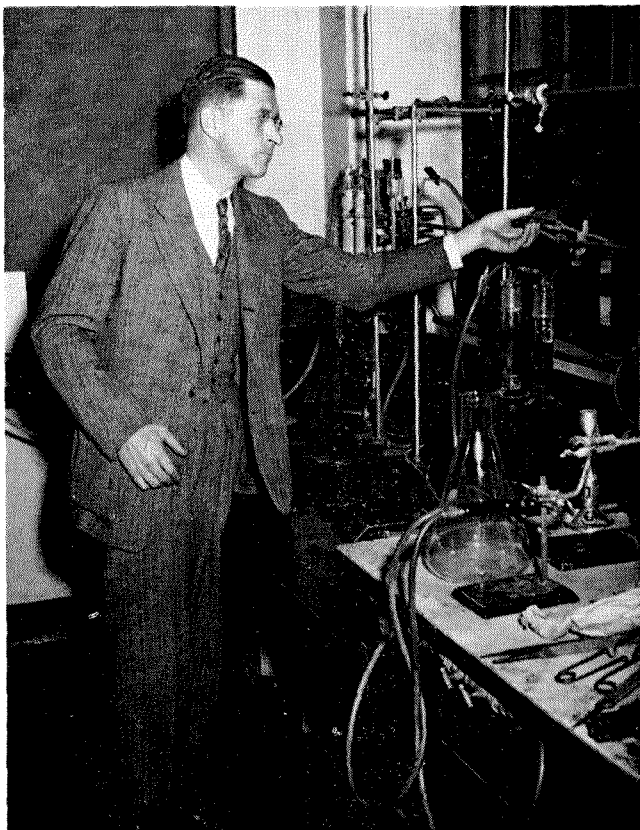
Dr. A. J. Haagen-Smit, Caltech Professor of Bio-organic Chemistry now on leave to work for the L.A. County Air Pollution Control District, manufactures smog in his laboratory above. Indistinguishable from the real thing, it's known, to his colleagues, as "Haagen-Smog."

combustion will be a partial oxidation which in many cases will approach a dry distillation when, as is often the case, not too much attention is paid to a sufficient supply of oxygen.

For one of the garbage materials, wood, we possess a thorough analysis of the distillation products. It has been shown that saturated acids—mostly acetic acid—are formed, accompanied by a few unsaturated acids and one with a furane ring. Also formed are alcohols, ketones, aldehydes, phenols and phenol ethers, ammonia derivatives and hydrocarbons of the benzene and furane series. In total, more than a hundred compounds were identified in these distillates.

These examples, incomplete as they are, suffice to show the complexity of the material released into the air. When these products are released and exposed to sun, air and water, drastic changes in the molecules take place, such as oxidation and polymerization.

This fact can easily be shown in the laboratory by exposing unsaturated hydrocarbons to the sunlight. Peroxides are formed, and iodine is liberated from potassium iodide solution which has been added to the oxidized hydrocarbons. This behavior is not limited to hydrocarbons. It has been shown to occur with a large number of organic compounds—alcohols, aldehydes and acids. These peroxides in turn are decomposed and

smaller aldehydes and acids are formed. The purifying action of the air will eventually break most of these compounds down to carbon dioxide.

An interesting experiment on the oxidation of unsaturated hydrocarbons can be performed by mixing two streams, one of dilute ozone and the other of small amounts of pure, unsaturated hydrocarbons or mixtures such as cracked gasolines. Where the two streams meet, a dense aerosol is formed. This shows some similarities to that observed in the Los Angeles area—as, for example, its oxidizing capacity, eye irritating effect, and its nearly neutral character.

This experiment presents a convenient way of preparing a type of aerosol quite different from that obtained with sulfur trioxide, and can be of help in the study of collecting techniques and analytical methods in this field. It also illustrates the possibility of a continuous chemical change of the products which one tries to determine. As soon as the ozonides are formed, the relatively unstable peroxides begin to decompose with the formation of more stable peroxides and the formation of acids and aldehydes. At the same time a considerable amount of polymerization takes place—probably the main cause of the formation of the dense aerosol. Also, the interaction of the products formed has been established, and we may therefore expect a rather complicated mixture in samples collected from air when unsaturated hydrocarbons have been released.

In such a case, the interpretation of the analytical results should be made with caution, and should take into consideration the possibility of conversions of the original products as well as the interaction of the components.

On the basis of the analytical work, the conclusion was reached that the oxidation of organic material—under the influence of sunlight and ozone, and possibly other air contaminants such as nitrogen oxides—plays an important role in the pollution of the atmosphere. In these reactions, aerosols are formed which have eye irritating properties and which, because of the small size of their particles, are able to decrease the visibility.

Support of these conclusions came in an unexpected way when the action of smog on plants was investigated. It had been observed that crops such as spinach, beets and grasses are often badly damaged when grown in this area. The symptoms are not identical with any observed in other areas, and are certainly different from sulfur dioxide damage.

Effect of smog on plants

In a project combining the efforts of the L. A. County Air Pollution Control District (LACAPCD), the University of California Agricultural Experiment Station at Riverside, and the California Institute of Technology an attempt was made to study the effect of smog and of individual air pollutants on plants.

It is fortunate (although not accidental) that the facilities at the Institute's Earhart Plant Laboratory are
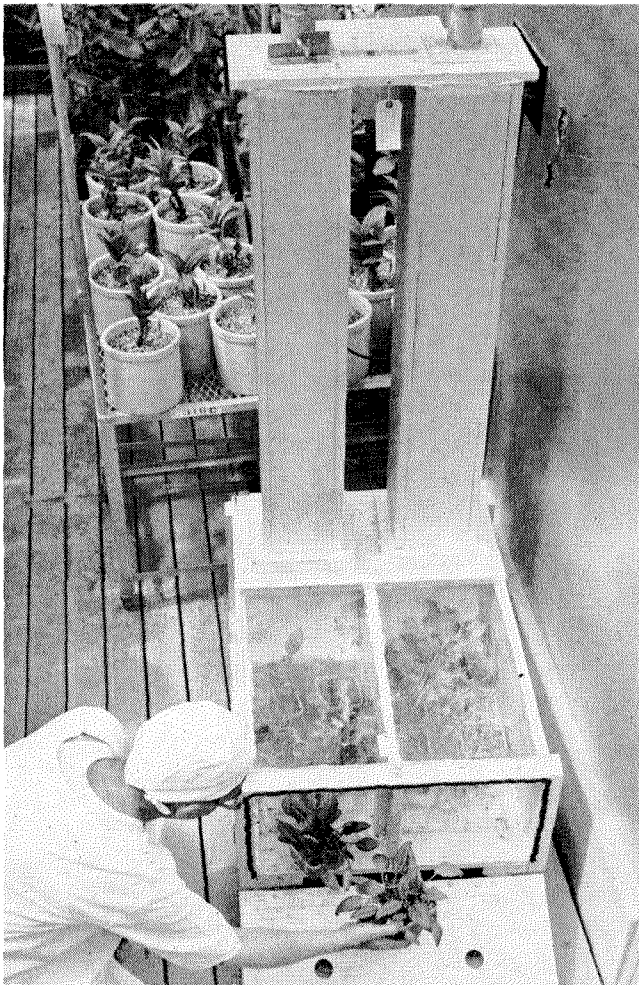
Smog damage to vegetables is studied at the Institute's Earhart Plant Research Laboratory. Smoggy air coming down the tunnel at the left, above, ruins plants. But the plants on the right keep healthy, since they're grown in air from which smog is removed by carbon filters.

ideally suited for studies of this kind. In this laboratory, rooms are available where the effect of gases on plants can be studied under closely controlled temperature and light conditions. Chemicals can be dispersed in these rooms either in gaseous form or as aerosols. The large turnover of air, amounting to 9,000 liters per minute, and proper distribution of the incoming and outgoing air make it possible to carry out quantitative determinations on chemical plant damage with considerable accuracy. Gas outlets provided in the doors permit the determination of the concentration of the gases used in the fumigation. The effect of a number of possible air pollutants was studied on a series of plants which were known to be susceptible to smog.

The smog indicator plants include spinach, sugar beet, endive, alfalfa and oats. The symptoms on the first three species are mainly silvering or bronzing of the underside of the leaf, whereas alfalfa and oats show bleaching effects. Some fifty compounds possibly present in the air were tested on their ability to cause smog damage— without success. However, when the reaction products of

ozone with unsaturated hydrocarbons were tried, typical smog damage resulted.

The ozonization was carried out in vapor phase by bringing the vapors of the hydrocarbons into contact with the ozone. When the two streams meet, a dense aerosol is formed which, through the adequate turbulence, is readily and evenly distributed in the room. As a source of the hydrocarbons ten-degree fractions of a cracked gasoline were used. (All gasoline now available is cracked, and contains 20 percent of olefins, or unsaturated hydrocarbons. The straight-run gasoline formerly used contained no more than 1 percent of olefins). It was found that the maximum of typical plant damage occurred with the oxidation products of low-boiling hydrocarbons.

After these encouraging results a series of pure olefins was tried in the ozone fumigation experiments. Maximum damage was found to occur with olefins of a chain length of five to six carbon atoms with the double bond in the end position.

Active agents in causing smog damage

During these oxidations a series of products are formed, with aldehydes and acids as end products. Fumigation experiments with these show that they are not responsible for the typical damage. We concluded, therefore, that the series of peroxides formed by the addition of ozone to the double bond are the active agents in causing the typical smog damage. Threshold determinations carried out on 1-n-hexene showed that oxidation of this hydrocarbon with a concentration of ozone as low as 0.05 parts per million still caused slight, but typical smog damage.

It is reasonable to assume that in our atmosphere where olefins are available, the ozone which occurs in unpolluted air in concentrations of 0.05-0.08 parts per million combines with hydrocarbons released in the area to produce material causing crop damage. However, the extent of the damage experienced when a smog wave hits the plants leads one to suspect that there are additional means by which oxidized hydrocarbons could be formed.

It has been shown that oil fractions acquire weed-killing properties when exposed to the action of sunlight and oxygen. Saturated as well as unsaturated hydrocarbons are thereby oxidized, yielding peroxides and their conversion products, aldehydes and acids.

Oxidizing the hydrocarbons

A third way of oxidizing the hydrocarbons was found in the plant experiments when oxides of nitrogen were used together with olefins. These oxides add to the double bond of the hydrocarbon and form nitrosates and nitrosites. Fumes are produced which can be eye-irritating when the reaction is taking place too violently, as in the case of butadiene, through the formation of nitro olefins. While the nitrosates and nitrosites are not causing plant damage at concentrations lower than one part

per million, one of the nitro olefins, nitroethylene (a very efficient lachrymator) did produce smog symptoms at concentrations of 0.1 part per million. The presence of this compound in the air has not been established, although there is evidence that some of the higher nitro olefins do occur, since we found small amounts of their polymers in the filter-paper extracts.

Since it was known that the nitrogen oxides may function as oxidation catalysts under the influence of light, plant fumigations were also carried out with nitrogen dioxide and the olefins under ultraviolet light. Typical smog damage was produced on the plants with both gasoline and 1-n-hexene. These symptoms can be produced readily in sunlight since, from chemical evidence, it is known that the upper limit of the photocatalytic action of nitrogen dioxide is at approximately 4300 A, a wavelength of light within the range of wavelengths received from the sun at the earth's surface. Under the influence of the light the reaction $NO_2 \rightarrow NO + O$ furnishes atomic oxygen which is available for the oxidation of the hydrocarbons.
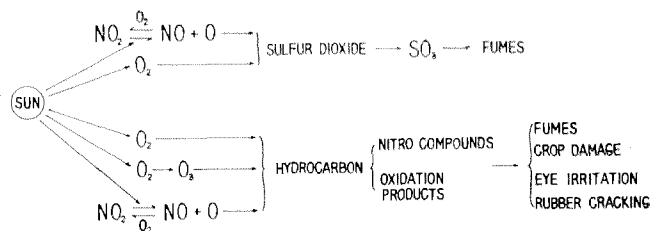
Smog effects on rubber

Supporting evidence for this NO_2 catalyzed oxidation came from a totally different aspect of the smog problem. Tire manufacturers had observed that rubber deteriorates faster in this area than in other parts of the country. The effects observed are rapid cracking when the rubber is stretched or bent during the exposure to the atmosphere. This effect was initially attributed to the ozone in the atmosphere. However, since it was shown that the high oxidizing value of the air was not due to the action of ozone, but to that of peroxidized organic material, it was necessary to find another explanation for this phenomenon. Dr. C. E. Bradley developed a technique to study rubber cracking by placing bent rubber strips in a measured stream of air. Under the conditions of the test, it takes half an hour to one hour to produce cracking on a non-smog day. When the smog is at a maximum, the cracking is visible after only seven minutes. This cracking effect can be compared with that caused by ozone. While, for example, on a normal day the concentration of "ozone" calculated in this way is 2-3 parts per hundred million, on a smog day calculations show that there should be 10 parts per hundred million of "ozone" in the air to give similar damage.

As in the plant experiments, many substances were tried without producing the typical cracking, and when it was found that the action of sunlight on hydrocarbons and nitrogen oxide gave plant damage, bent rubber samples were exposed to a similar action. The results of these tests showed that cracking of rubber similar to that caused by ozone could be produced. In this case, the rubber, being an olefin, functioned as did the lighter unsaturated hydrocarbons in the plant experiments, as acceptor of the oxygen.

The evidence from these different lines of research all points to the presence of peroxidized compounds, and a direct demonstration of their presence can be made when enzymatic reactions are used. Peroxidase is able to oxidize a number of amines and phenols to colored compounds only when hydrogen peroxide or alkyl peroxides are present. This reaction is readily given by condensates collected from the air in traps cooled with liquid oxygen. This peroxidase reaction and the coloring of the reagent is prevented by poisoning the enzyme with hydrogen cyanide, thereby establishing that the color is not due to a non-specific oxidation, but to the enzymatic action of the peroxidase.

As a result of this work we have come to the conclusion that the organic material, mostly hydrocarbons, released into the air is oxidized by the ozone initially present; by the action of oxygen and sunlight; and by the catalytic action of the NO_2 and NO cycle releasing atomic oxygen under the influence of the sunlight. These oxidations produce peroxides, aldehydes and acids, and aerosols are formed which decrease visibility and would be a source of eye irritation. In addition, side reactions such as the addition of the nitrogen oxides to the double bonds might occur, giving rise to aerosols, as well as eye irritants. These reactions are incorporated in the following scheme:

$$NO_2 \underset{}{\overset{O_2}{\rightleftharpoons}} NO + O \longrightarrow \text{SULFUR DIOXIDE} \longrightarrow SO_3 \longrightarrow \text{FUMES}$$

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$$O_2 \quad O_2 \rightarrow O_3 \longrightarrow \text{HYDROCARBON} \begin{cases} \text{NITRO COMPOUNDS} \\ \text{OXIDATION PRODUCTS} \end{cases} \longrightarrow \begin{cases} \text{FUMES} \\ \text{CROP DAMAGE} \\ \text{EYE IRRITATION} \\ \text{RUBBER CRACKING} \end{cases}$$

$$NO_2 \underset{O_2}{\overset{}{\rightleftharpoons}} NO + O$$

For a total picture of the air pollution problem, the presence of inorganic materials cannot be neglected. Such a contribution we find in the SO_2, which through its oxidation with sunlight and oxygen will decrease the visibility. Undoubtedly the catalytic action of the NO_2 with light plays an important role, as in the case of the oxidation of the organic material. Through the combined efforts of the enforcement agencies as well as industry, this source of pollution has been greatly reduced, as has that of metallic dusts.

Where we go from here

With these ideas on the causes of the smog nuisance, the smog elimination has entered a new phase. Careful studies have to be made of the amounts and nature of the organic material released into the air. In this way we can hope to make up a balance sheet on which all the deposits of the contributors are listed. Only in this unemotional way can we hope to bring relief to this area.