

SMOG RESEARCH PAYS OFF

By A. J. HAAGEN-SMIT

OLD TIMERS in this area tell us how, on clear days, they used to be able to see Catalina Island from their houses in the foothills. Now, we talk about a nice clear day when we see only five to ten miles away.

A decrease in visibility is to be expected when so many people congregate in an area, but during the war years a few objectionable features were added. A peculiar smell developed—sometimes reminiscent of bleachpowder, sometimes of ozone, but usually with such an individual character that it is referred to as smog odor. Because of the great sensitivity of our sense of smell we can spot this odor long before a dense haze reduces the visibility to less than half a mile, and eye irritation begins to be felt.

To these effects were added throat and nose irritation. Farmers noticed a peculiar damage to their leafy vegetables. Gardeners became aware of the yellowing of newly seeded lawns. And rubber manufacturers became concerned about the pronounced rubber cracking observed in the area.

It was some time before the public became sufficiently aroused and demanded that something be done about this air pollution problem. In 1947 an organization was formed which could study the problem regardless of city limits, and which was given the legal tools to enforce the measures necessary for improving the situation. This organization now functions as the Los Angeles County Air Pollution Control District.

There were plenty of opinions on how to attack the problem. At one end of the scale were those who did not see the use of any research. Their philosophy was, "Where there's smoke, there's smog." At the other end of the scale were those who wanted to postpone taking any restraining measures at all until research had definitely established which particular sources contributed to the smog nuisance and whether they could be called health hazards.

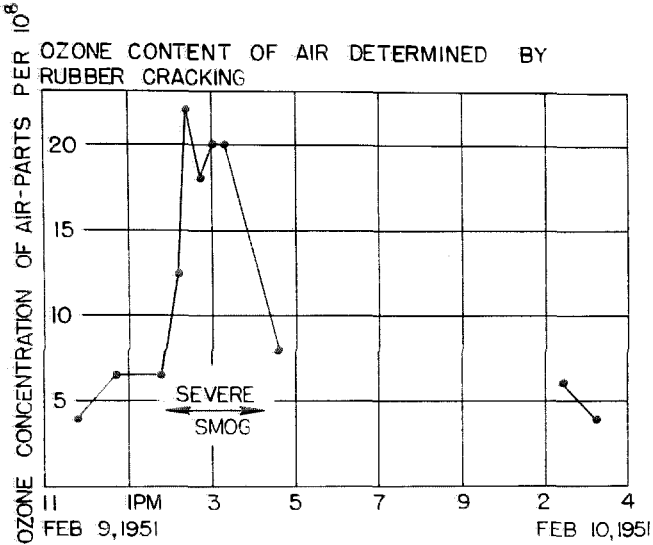
Fortunately for those suffering from smog, the newly

founded District, under the guidance of Dr. Louis C. McCabe, decided that obvious sources of smoke and fumes should be controlled, and that—parallel to this program—research should be carried out on the chemical analysis of the air to discover the presence of any unknown pollutants.

This program has been carried out with great vigor by Dr. McCabe's successor, Mr. Gordon P. Larson. Dust and fumes from numerous sources have been reduced to the level they were at before 1940. Although some improvement was noticeable after these known sources were for the most part controlled, dense smog continued to roll over Los Angeles and its environs. The answer to this puzzling problem has been given by research on smog.

This research was carried out at the District Laboratory and, in addition, contracts were made with the California Institute of Technology, the University of California, Chaney Laboratories, the Bureau of Mines, the Bureau of Standards, and Beckman Instruments, Inc. In this way, experts in the field of analysis, plant physiology, instrumentation, meteorology and aerosols were mobilized in an attack on the problem.

It was found that the most characteristic chemical property of the Los Angeles air during a smog period was the oxidizing capacity demonstrated in the release of iodine from neutral buffered potassium iodide solutions. The presence of peroxides of organic nature was postulated, and it was reasonable to assume that these could originate in oxidation processes of organic material in the air with other air constituents, such as ozone and nitrogen oxides. These reactions were demonstrated by a vaporphase oxidation of unsaturated hydrocarbons with ozone and with nitrogen oxides. When a cracked gasoline was used as a source of olefins, aerosols were produced which were eye-irritating and which also simulated the smell usually associated with Los Angeles smog.



Rubber cracks faster as smog becomes more severe

Evidence that these reactions play a role in the Los Angeles smog problem came from the study of rubber cracking and crop damage in this area. It has long been known that ozone has a characteristic cracking action on raw or vulcanized rubber when the rubber is under strain in a bent or stretched condition. Low concentrations of ozone are used commercially for comparative tests on rubber compounds, but when a standardized rubber is used, this method can serve as a sensitive measure for ozone concentration. The normal cracking time in the Los Angeles area on smog-free days is 40-60 minutes, corresponding to 0.02-0.03 parts per million of ozone. On a severe smog day values as high as 0.22 parts per million have been measured, corresponding to an initial cracking time of only six minutes. In this case, the cracking time of the rubber was determined every hour, and the corresponding ozone values plotted (above). The sharp rise shown on the chart corresponds closely to the subjective judgment of the severity of the smog. Enzymatic methods have shown that the peroxides—the reaction products of ozone and organic material—show a similar rise during the smog period.

An important contribution to the understanding of the chemistry of the Los Angeles smog was made by the study of crop damage in a cooperative enterprise of the Los Angeles County Air Pollution Control District, the California Institute of Technology and the University of California. For the determination of the crop damaging materials present in the air, five different plants were used—spinach, beets, endive, oats and alfalfa. The smog symptoms on these indicator plants are the production of a metallic sheen on the lower surface of leaves on spinach, sugar beets and endive; yellowing of oats; and a bleaching of the leaves of alfalfa, producing an oak leaf pattern. These varied symptoms distinguish this damage from the effect of previously known toxic materials.

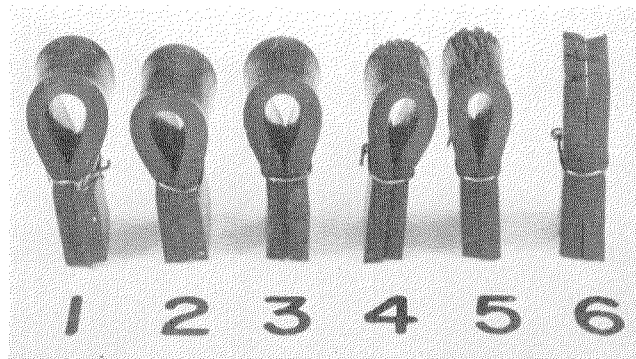
In view of the strong oxidizing action of the smog,

and the suspected presence of considerable amounts of easily oxidizable material from petroleum products, fumigations were carried out with ozone and vapors of a cracked gasoline. The development of the damage symptoms, such as oiliness of the underside of the leaves of spinach and endive after a few hours of fumigation, as well as the further development of the symptoms on all five indicator plants, was indistinguishable from that noticed on plants exposed to smog.

To establish the nature of the agent responsible for the damaging effects, the gasoline was distilled in ten-degree fractions and these were released in a fumigation room together with ozone. Maximum damage was obtained with the fractions boiling between 39 and 69 degrees Centigrade. These results are shown in Chart A (p. 13), in which the estimated degree of damage is plotted against the average boiling point of the gasoline fractions used in the fumigations. A prerequisite for this effect is the presence of a double bond. However, the size of the molecule has a pronounced influence on the severity of the reaction. In fumigation with ozone and homologues of ethylene, optimum plant damage is observed with olefins of 5 and 6 carbon atoms, as can be seen in Chart B.

The concentration of ozone at which damage occurs with the olefins is well within the range of the ozone concentrations found in the atmosphere. In fumigation experiments with ozone a series of oxidation products is formed. The primary product, the ozonide—itsself a peroxide—undergoes a series of changes leading to other peroxides and finally to aldehydes, ketones and organic acids. It has been shown that the active agent must be found in the peroxides formed as intermediates in the oxidation of the hydrocarbons.

In addition to ozone there is another powerful oxidation agent in the smog atmosphere: the nitrogen oxides. These oxides, under the influence of light, rapidly oxidize organic materials. To study these reactions, a fumigation room was built from Plexiglass, which permits the use of practically the entire spectrum of the sun available to the lower regions of the atmosphere. When a cracked gasoline was released in the presence of nitrogen oxides and sunlight, typical smog damage on plants was observed. In addition, characteristic smog odor and eye irritation were apparent.



Ozone in air is measured by effect on rubber under strain. Degree of cracking indicates concentration.

In order to determine the nature of the hydrocarbons which, upon oxidation, are responsible for the eye irritation, ten-degree fractions of gasoline were used, while the oxidant was adjusted to 0.4 ppm. of nitrogen dioxide and 0.2 ppm. of ozone. These conditions duplicate those present in the atmosphere during smog conditions.

Observers sensitive to eye irritation on smog days compared their reactions in these fumigations with those experienced under conditions of natural smog. In experiments with concentrations of 1.6 ppm. of gasoline fractions the eye irritation was definite in the range of 50 to 80° C., as shown in Chart C. A comparison of Charts A and C shows that maximum plant damage and eye irritation occur in about the same boiling-point region of the gasoline fractions. Eye irritation is, however, observed also in fractions with boiling points below 35° C.

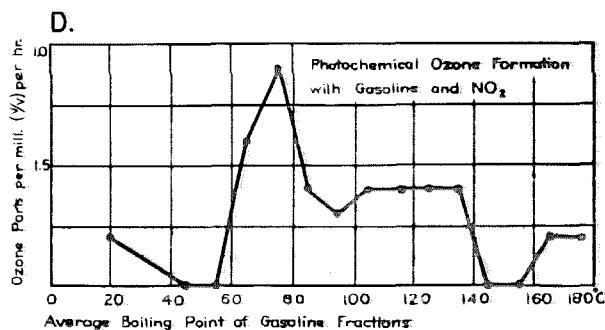
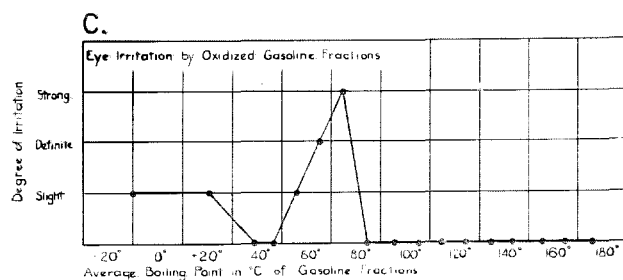
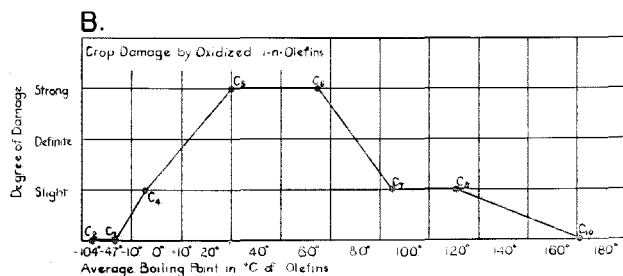
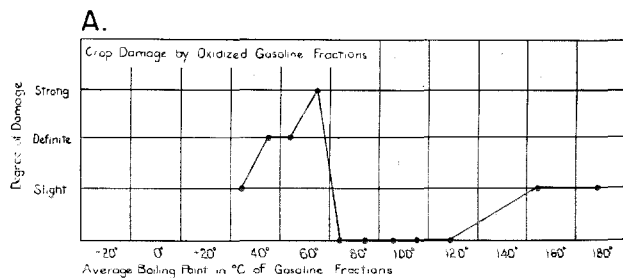
These findings were confirmed with pure olefins, and definite smog effects were obtained with concentrations as low as 0.2 ppm. of hydrocarbon. As in the crop damage experiments, the irritating agent consists of peroxides; the end products of the oxidation—aldehydes and acids—cannot be responsible for the irritating action since their concentrations, even upon complete conversion of the hydrocarbons, are considerably lower than those required for irritation.

Experiments in the fumigation house using NO₂ and O₃ and sunlight for the oxidation of the gasoline fractions have shown that within a few minutes a haze develops. These effects are especially noticeable with ring compounds with a double bond in the ring. Experiments on the oxidation of di-cyclopentadiene and indene in the presence of NO₂ (nitrogen dioxide), O₃ (ozone) and sunlight have shown that in a concentration of 50 parts per million of hydrocarbon a blue haze completely obscuring the vision over a distance of only eight feet fills the room. Even at 10 ppm. the blurring of objects is already noticeable over this short distance.

A large part of the aerosol droplets collected from the air have been shown to be of an oily nature, and the chemical analysis has shown that their composition resembles that of droplets found in the artificially produced aerosols of oxidized hydrocarbons.

Parallel with these investigations, the analytical work carried out on samples of pollutants collected on filters and in bubblers has shown the presence of the more stable end products of the reactions mentioned above. In the hands of Dr. Martin Shepherd of the National Bureau of Standards, the mass spectrograph gave valuable information on the multitude of hydrocarbons present in the Los Angeles air, and in addition he was able to show the similarity between the artificially oxidized mixtures of hydrocarbon and that occurring in smog.

The most puzzling property of the smog air, the high oxidizing capacity, remained to be solved. This oxidant, calculated as ozone, amounts to 0.5 - 0.6 ppm. on severe smog days. This oxidant is measured by iodine release



Experimental Crop Damage (Charts A and B), Eye Irritation (Chart C) and Ozone Formation (Chart D)

from neutral buffered KI (potassium iodide) solutions and a large part of the iodine release is due to the presence of nitrogen oxides, which, in the concentrations at which they occur in the Los Angeles atmosphere, oxidize the KI solution. The more interesting fraction of the so-called total oxidant of smog is that which closely simulates the behavior of ozone in giving typical rubber cracking. This fraction was shown to rise during severe smog, and, in the standardized rubber cracking test mentioned earlier, cracking times of six minutes were observed, corresponding to an ozone concentration of 0.22 ppm. The natural ozone concentration on the earth surface is reported to be of the order of 0.02-0.03 ppm.

These values were confirmed by using the rubber cracking test in unpolluted desert and beach areas. It is unlikely that additional ozone could be drawn

from the higher atmosphere when the presence of inversion conditions characteristic of smog conditions prevents this free exchange. Further evidence against such a possibility is presented by the nearly complete absence of rubber cracking at night. This observation points to photochemical processes in the formation of the rubber cracking material.

Rapid rubber cracking comparable to that observed during smog periods was observed during the plant fumigation experiments with nitrogen oxides and sunlight only in the presence of organic material, such as hydrocarbons.

When gasoline fractions are used in concentrations of 0.1 to 1 ppm, the presence of 0.4 ppm. NO_2 , rapid cracking occurs in the same boiling-point region in which the most intense crop damage has been found, as shown in Chart D on page 13. This effect on rubber was confirmed by the use of branched saturated hydrocarbons and olefins as well as their oxidation products: alcohols, aldehydes, ketones and acids. The rubber cracking material was isolated and identified as ozone.

It is interesting to note that the most marked ozone formation in oxidation of gasoline fractions occurs in the same boiling point region where the most extensive crop damage and eye irritation have been observed, and we conclude that ozone formation and peroxide formation are closely related phenomena. In many of these oxidations we have shown that the amount of ozone formed is many times greater than that of the organic material or the nitrogen oxides present, and we have to conclude that ozone is formed in a chain reaction.

The photochemical dissociation of NO_2 with sunlight provides a continuous source of atomic oxygen for this reaction, since NO_2 is regenerated through oxidation of NO by molecular oxygen. It is postulated that in the chain reaction leading to ozone formation, peroxide radicals are formed which react with molecular oxygen to form ozone. After the peroxide radical has released one of its oxygen atoms, it may be reoxidized and again react with molecular oxygen.

To test this hypothesis the photochemical oxidation of diacetyl was studied, since it is known that diacetyl under the influence of light easily forms free radicals. In this experiment the addition of NO_2 is not necessary for the transfer of light energy, since diacetyl absorbs light in the visible range of the spectrum. Diacetyl in concentrations of 2000 ppm. in a 2 liter flask gives rapid rubber cracking, and in half an hour the concentration of ozone has reached 30 ppm. The lowest concentration of diacetyl at which cracking of rubber could be observed was 40 ppm.

It has been proven by isolation and chemical identification that ozone was also formed in this case. These findings were confirmed by mass spectrographic measurements carried out by the Consolidated Engineering Corporation. Rubber cracking without the addition of nitrogen oxide is observed when butyl nitrite is exposed to light. It is known that, in the absence of oxygen, alkyl radicals and nitrogen oxides are formed by the

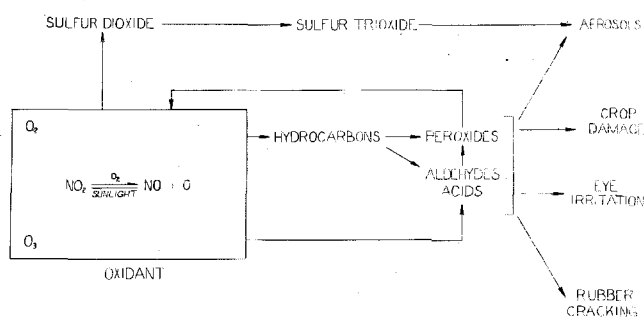
decomposition of butyl nitrite. Our expectation that, in the presence of oxygen, ozone would be formed, was confirmed by the rapid rubber cracking observed.

In the photochemical oxidations with nitrogen oxides, ozone formation up to several parts per million has been demonstrated with concentrations of air pollutants of the same order of magnitude as those found in the smog atmosphere. The abnormally high ozone content of smog air, and consequent severe rubber cracking during such a period, is therefore readily accounted for by the ozone formed in these reactions.

The experimentally demonstrated ozone formation in air containing hydrocarbons or their oxidation products, and nitrogen oxides under the influence of sunlight, establishes a definite relation between the major nuisances observed during a smog period and is strong evidence of their common origin.

On the basis of experiments it is possible to condense the major features in the development of irritating and nuisance effects in the Los Angeles atmosphere, as shown in the diagram below. The oxidant is represented by a complex of factors consisting of atomic oxygen formed by the photochemical dissociation of nitrogen dioxide and ozone produced in the photochemical oxidation of organic material. The oxidant reacts with hydrocarbons and their oxidation products, producing peroxides and further degradation products. The arrow leading from the peroxides to the oxidant indicates the participation of these compounds or their radicals in the formation of ozone. Included in the general picture is the oxidation of sulfur dioxide to sulfur trioxide as a contributor to the decrease in visibility. This oxidation is known to be catalysed in the presence of nitrogen oxides, which are released at the same time in combustion processes.

As a result of the teamwork initiated by the Los Angeles Air Pollution Control District the major cause of the smog has been recognized. The problem of crop damage, eye irritation, haze, smell and ozone formation has been brought to a practical solution. All these phenomena are due to the same cause—the emission of large quantities of hydrocarbons and nitrogen oxides to the air. The District has not hesitated to follow up the conclusions which could be drawn from the research studies. An intense source study has been made of all major contributors of organic material and of nitrogen oxides to the air.



Atmospheric reactions in smog formation

The Second Technical and Administrative Report from the Los Angeles Air Pollution Control District reveals that approximately 2,000 tons of hydrocarbons and 250 tons of nitrogen oxides are lost to the air daily.

The nitrogen oxides are released in all combustion processes and have nearly doubled since 1940. This is also true for the type of hydrocarbons which have been shown to be mainly responsible for the nuisance effects of smog: olefins and branched saturated hydrocarbons.

The main reason why nuisance symptoms developed during the war years is to be found in the revolutionary change in the composition of gasoline. The diagram at the right shows the difference between old and new gasoline. The nonreactive paraffins in straight run gasoline have been replaced in the cracking process by paraffins with branched chains and by olefins. Both groups of compounds are readily oxidized and lead to the formation of peroxides and ozone, thereby producing all of the typical smog nuisance effects.

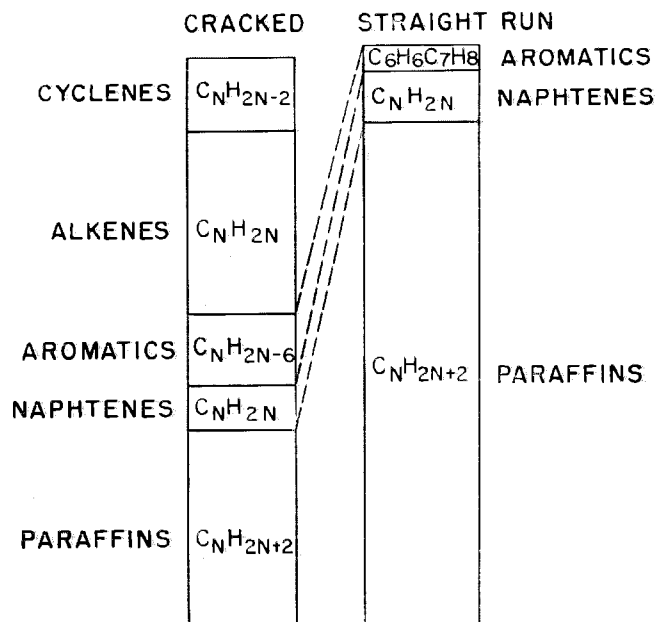
The cracking process gives a much higher yield of gasoline from crude oil than the old distillation process. With the enormous increase in the demand for gasoline it is not economically feasible to go back to the old process. Until changes in the composition of the present-day gasoline have been made it is necessary to handle modern gasoline as a potential irritant, and losses have to be prevented wherever possible.

Skimming ponds at the refinery, baking in the sun, lose considerable quantities of volatile material. Old-fashioned storage tanks, warming up in the sun, expel additional hydrocarbons. Such devices belong to the past, and will undoubtedly be replaced by separatory tanks and floating tanks.

Following the distribution of gasoline to the consumer, there are losses involved in filling tank cars, gasoline storage tanks at filling stations, and finally, the tanks of automobiles. These losses are considerable, as a rough calculation shows. When a gasoline tank of an automobile is filled, 15 gallons of vapor are replaced with liquid. Usually we don't give any thought to this loss. Per car filling, it amounts to the loss of about 1/10 of a gallon, or 2.5 cents. This seems a small amount, but since 2.5 million gallons of gasoline are used daily in the Los Angeles area, then 2.5 million gallons of vapor are lost in the filling of cars alone—a release of 50 tons daily.

Similar losses have occurred when the gas station filled its tanks, when the tank car was filled, etc. If we assume some four of these transfers, 200 tons of gasoline are lost to the air. The engineering difficulties do not seem too great to overcome such a loss, at least at the marketing installations.

More difficult to solve will be the problem of incomplete combustion in the automobile. More efficient combustion, especially during acceleration and deceleration, might be possible. Some proposals have been made, suggesting the combustion of the unburned fuel in a separate unit. Such ideas are, however, still in the experimental stage, and we can hardly expect results

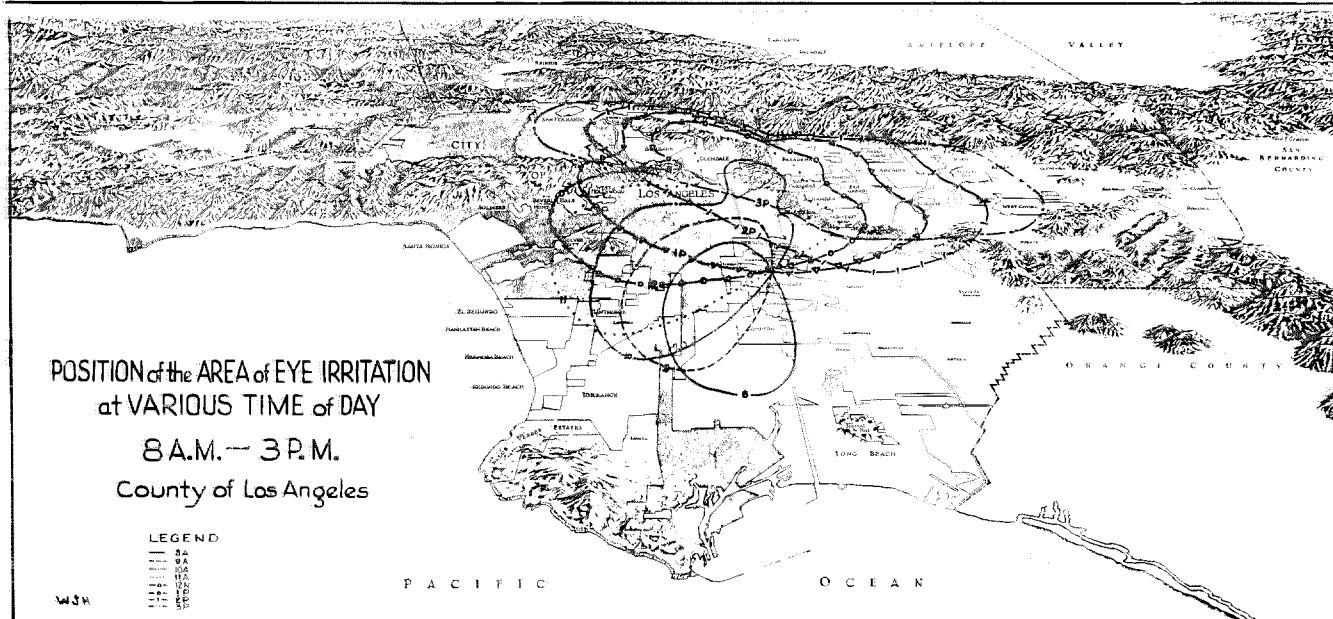


Comparison of old and new gasoline shows the factors responsible for making cracked gasoline a potential irritant

of such inventions in a few years. Since most of the hydrocarbons are released during deceleration, downtown traffic with its many stop signs contributes materially to the hydrocarbon losses. The construction of freeways, as is now going on in Los Angeles, will help in cutting down the losses. Efficient community transportation will eventually replace much of the nerve-racking traffic of today, and a considerable reduction in the use of fuel, as well as in air pollution, can be expected.

Estimates made by the L. A. County Air Pollution Control District show that nearly equal quantities of hydrocarbons are lost by automobiles and by the petroleum industry—the combined total amounting to 2,000 tons daily. From such computations one could draw the conclusion that automobiles and the petroleum industry are about equal contributors to the smog condition. However, in these compilations of data the time and place of release of the hydrocarbons and their oxidation products do not appear. Smog is experienced only during part of the day. In Pasadena, the mountains disappear from view in the early afternoon, and reappear after a few hours. At the County Air Pollution laboratory at 52nd Street and Santa Fe Avenue, the smog wave arrives in the morning and leaves in the afternoon. The very existence of a smog wave shows that the whole Los Angeles area does not produce smog in equal density.

The movement of the smog cloud over this area is well illustrated by a map (p. 16), made by the District, plotting the density of telephone complaints on a smog day. The area of greatest pollution, first recorded at 8 o'clock in the morning, slowly moves northward and squeezes through the gaps in the low mountain range separating Pasadena from the Los Angeles area and at 3 o'clock has covered San Fernando and the San Gabriel Valley.



The most reasonable explanation of this phenomenon seems to me the sudden release of hydrocarbons from the relatively small refinery area shortly after sunrise, when tanks are warming up and skimming ponds are rapidly beginning to lose a major part of their daily contribution, which has collected and remained unvolatilized during the cool night.

On the other hand, the automobile operates during the whole day, and therefore spreads its contribution more evenly during that time. In addition, the loss is spread over a far larger area than that from the oil industry. Consequently, we can expect a relatively high concentration of hydrocarbons originating in the small refinery area, superimposed on a more evenly distributed lower concentration from automobile exhaust gases. With wind velocities of 4-5 miles per hour, the pollutants slowly move north, and we should expect to see the smog cloud approaching at about 9 o'clock at the County laboratory, and at noon in Pasadena.

During that time, ample opportunity exists for the oxidation of the hydrocarbons. Power plants, industries and automobiles furnish a continuous supply of nitrogen oxides for the photochemical oxidation and formation of ozone. The smog wave will be materially reduced through control measures now being taken by the petroleum industry. There is, however, a great deal more to be done.

We should realize that in each case of air pollution it is not very likely that 100 percent reduction can be achieved. A reasonable balance has to be found between what is desirable and what is economically feasible. About 600 tons of SO_2 were being released daily before the refineries decided to convert some part of it to sulfur. At present, about 300 tons are still going into the air, not from the refineries, but from fuel burners, automobiles, etc. Since this pollution is not confined to a major industry but is released in millions of small combustions,

we have reached a situation whereby it is difficult to remove any additional SO_2 from the air. Fortunately, the SO_2 concentration has dropped to such a level that it rarely exceeds 0.1 ppm., which cannot be considered harmful.

The same situation is true for dusts and fumes of a miscellaneous group of industries. Control devices have been installed in many of them. None of these are 100 percent effective, and the allowable emissions are set after considerable study and discussions of the economic possibilities.

It is clear, therefore, that every new industry, and every person entering this area, is going to add to the existing air pollution. With the increase in population and the advent of new industries the problem of smog control becomes increasingly difficult. Already the District has studies underway on the possibility of zoning for air pollution purposes. Fortunately there are definite signs that we are on the road to cleaner air. The activities of Los Angeles Air Pollution District and of the industries have brought many of the emissions to pre-war level and a good start has already been made on the recovery of the major cause of the smog: the hydrocarbons.

Gradually the frequency with which the dense smog is annoying us will become less and less. Eye irritation and crop damage will be the first symptoms to disappear. The visibility will undoubtedly improve, but there will remain the contribution from individual sources like the automobile and the incinerator, so that the District must call on all of us to cooperate in the fight for clean air.

In view of the outstanding achievements of the Los Angeles County Air Pollution Control District, we help ourselves when we give this law-enforcing agency our wholehearted support in eradicating the smog nuisance completely. Smog is on the way out; let us speed up its departure and let us keep it out.