SMOG CONTROL

— Is it just around the corner?

by A. J. Haagen-Smit

Old timers, which in California means people who have lived here some 25 years, will remember the invigorating atmosphere of Los Angeles, the wonderful view of the mountains, and the towns surrounded by orange groves. Although there were some badly polluted industrial areas, it was possible to ignore them and live in more pleasant locations, especially the valleys. The ideal climate and scenery started an influx of people which has now reached some 200,000 persons per year. But with this booming prosperity, the more subtle attractions began to disappear. Haze over large areas, limiting the view, became an everyday occurrence, and was the first indication that something was wrong with our atmosphere.

In 1942, just 20 years ago, the community was disagreeably surprised when the atmosphere was filled with a foreign substance that produced a strong irritation of the eyes. Fortunately, this was a passing interlude which ended with the closing up of a wartime synthetic rubber plant. However, this event clearly showed that it is not possible to emit unlimited amounts of foreign materials into the atmosphere without affecting the quality of the air. A few years after this first warning, the community was again stirred by serious complaints about strange-smelling, irritating clouds. These complaints resulted in the formation of the Los Angeles County Air Pollution Control District, which is governed by the County Board of Supervisors.

The APCD took on a big job, for by now the county's 4,003 square miles houses some 77 incorporated cities, the population has doubled since 1930, and industrial plants have boomed to more than 17,000 in 1962.

In its first years, the APCD placed special emphasis
Air pollution control has resulted in a reduction of dustfall in the Los Angeles basin to the 1940 level.

on the control of visible sources of pollution, smoke and fumes, and sulfur dioxide. By 1955 most of these were controlled and thousands of tons of pollutants were prevented from entering the air. Scavenger plants now recover several hundreds of tons of sulfur compounds originating from processing of crude oil at the refineries. Steel factories and foundries use electrostatic precipitators, bag filters, and scrubbers to collect their dusts. As a result, the dustfall in this area has decreased markedly (above).

Further reductions in the emission of sulfur compounds have been obtained by restricting the use of sulfur-containing fuel during seven months of the year, from April 15 to November 15, and during days in which atmospheric conditions would be likely to lead to higher smog levels. Monitoring of the atmosphere by chemical and spectrographic methods shows clearly the effect of burning sulfur-free gas instead of oil in power plants. The lowering of the $\text{SO}_2$ concentration in the air during the smog season is shown below.

To date, control efforts at a cost of more than 100 million dollars have resulted in preventing 5000 tons of air contaminants from entering our atmosphere each day.

Although the stringent control did reduce dustfall and gave some improvement in visibility and local nuisance problems, it did not give relief from the regular smog symptoms - eye irritants, plant damage, excess cracking of rubber articles, and the peculiar odor. The control of the visible sources emphasized that there was something other than smokestacks which gave rise to the smog symptoms.

Through investigations initiated at Caltech, we know that the main source of this smog is due to the release of two types of material. One is organic material - mostly hydrocarbons from gasoline - and the other is a mixture of oxides of nitrogen. Each one of these emissions by itself would be hardly noticed. However, in the presence of sunlight, a reaction occurs, resulting in products which give rise to the typical smog symptoms. The photochemical oxidation is initiated by the dissociation of $\text{NO}_2$ into $\text{NO}$ and atomic oxygen. This reactive oxygen attacks organic material, resulting in the formation of ozone and various oxidation products. Some of these products, peracetyl nitrate and formaldehyde, are eye irritating. Plant damage is caused by peracetyl nitrates and also by ozone. The oxidation reactions are generally accompanied by haze or aerosol formation, and this combination aggravates the nuisance effects of the individual components of the smog complex.

For smog control purposes, it is of importance that olefins, most saturated hydrocarbons, aromatics, and derivatives of these various types of organic material form ozone and one or more of the other typical smog manifestations. Control methods are therefore concerned with the emissions of volatile organic materials and with the other component of the smog reaction, the oxides of nitrogen.

These organics are emitted from the incomplete combustion and evaporation of gasoline in motor vehicles, from the losses of the petroleum industry, and from the use of solvents. A source survey conducted by the APCD in 1951 showed that the losses by the petroleum industry were quite substantial. Subsequent control, mainly at the refineries, has reduced these emissions by about 80 percent to 85 tons of organics per day, as determined in an elaborate survey by representatives of federal, state, and county government.

The significant reduction, however, was offset by...
an increase in the emission by motor vehicles. In 1940 there were about 1.2 million cars in the metropolitan area of Los Angeles. By 1950 there were 2 million. Today there are three and a half million. These three and a half million cars, including busses and trucks, burn about 6 million gallons of gasoline per day and emit 1300 tons of hydrocarbons, 600 tons of oxides of nitrogen, and 6500 tons of carbon monoxide per day. A glance at the table below shows that these emissions outweigh those of other sources.

<table>
<thead>
<tr>
<th>Source</th>
<th>Organics</th>
<th>Oxides of nitrogen</th>
<th>Carbon monoxide</th>
<th>Subulate Aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>automobiles</td>
<td>750</td>
<td>450</td>
<td>5000</td>
<td>20</td>
</tr>
<tr>
<td>evaporation</td>
<td>150</td>
<td>150</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>exhaust</td>
<td>150</td>
<td></td>
<td>1500</td>
<td>5</td>
</tr>
<tr>
<td>trucks, buses</td>
<td>10</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>evaporation</td>
<td>10</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Dissel</td>
<td>10</td>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>aircraft</td>
<td>10</td>
<td></td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Moving Sources</td>
<td>1300</td>
<td>600</td>
<td>7000</td>
<td>30</td>
</tr>
<tr>
<td>Petroleum Industry</td>
<td>250</td>
<td>1</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Organic Solvent Uses</td>
<td>400</td>
<td></td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Combustion (Sting Months)</td>
<td>10</td>
<td>200</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Miscellaneous Industries</td>
<td>50</td>
<td>15</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Stationary Sources</td>
<td>700</td>
<td>200</td>
<td>250</td>
<td>100</td>
</tr>
<tr>
<td>All Sources</td>
<td>2000</td>
<td>800</td>
<td>7000</td>
<td>300</td>
</tr>
</tbody>
</table>

It is clear that the five percent increase in emissions from automobiles per year will make smog conditions worse unless something drastic is done to reverse this trend.

Emission of hydrocarbons occurs at several places in motor vehicles. Incomplete combustion of gasoline allows unburned and partially burned fuel to escape from the tailpipe. Seepage of gasoline, even in new cars, past piston rings into the crankcase, is responsible for "blowby" or crankcase vent losses. Evaporation from carburetor and fuel tank are substantial contributions, especially on hot days.

The exhaust gases of gasoline-powered motor vehicles consist mainly of nitrogen, oxygen, carbon dioxide, and water vapor. In addition, there are lesser quantities of carbon monoxide, hydrogen, hydrocarbons, partially oxidized hydrocarbons, oxides of nitrogen and of sulfur. The smoke particles contain carbon, lead salts, oil, and other non-volatile matter. In combustion a mixture of fuel and air is drawn into the cylinder. For complete combustion the relative proportion of air and gasoline, the air-fuel ratio, is around 15 to 1. To obtain smooth operation and maximum power, a mixture containing more gasoline is provided and consequently not all of the gasoline can be burned in the various operation cycles of the engine.

The greatest concentration of incompletely burned hydrocarbons occurs during the deceleration cycle. When fuel is drawn in but little or no air is supplied for combustion, unburned fuel is vented to the outside. However, to assess the actual contribution of each driving cycle, we have to know the exhaust volumes, which vary from a few cubic feet per second for idling and deceleration to 50 to 100 cft per second for acceleration and cruising. In addition, we have to take into account the time spent in each of these cycles in town driving.

The table below gives the relative weights of exhaust emissions for the different operation cycles, on an average trip in Los Angeles County, for hydrocarbons, carbon monoxide, and oxides of nitrogen. The emission of oxides of nitrogen during these cycles is especially pronounced during acceleration and cruising since their formation is promoted by high temperature and increase of oxygen. We find low concentrations of oxides of nitrogen, therefore, in idling and deceleration, while high values are found during cruising and acceleration.

### Relative Contributions of Exhaust Components in Operation Cycles in Weight Percentages

<table>
<thead>
<tr>
<th>Driving cycle</th>
<th>Hydrocarbon emission</th>
<th>Carbon monoxide emission</th>
<th>Oxides of nitrogen emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Idling</td>
<td>5</td>
<td>10</td>
<td>.5</td>
</tr>
<tr>
<td>Acceleration</td>
<td>55</td>
<td>60</td>
<td>80.</td>
</tr>
<tr>
<td>Cruising</td>
<td>15</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Deceleration</td>
<td>25</td>
<td>15</td>
<td>2</td>
</tr>
</tbody>
</table>

The preferred method of control of the tailpipe hydrocarbon emission is a better combustion in the engine itself. (The automobile industry has predicted the appearance of more efficiently burning engines in 1965. It is not known how efficient these will be, nor has it been revealed whether there will be an increase or decrease of oxides of nitrogen.) Other approaches to the control of the tailpipe gases involve completing the combustion in muffler-type afterburners. The two main types are shown below.

Two methods of controlling hydrocarbon emission from automobile tailpipes through combustion of the exhaust gases—a catalytic afterburner (left) and a direct-flame afterburner (right).

November, 1962
One type relies on the ignition of the gases with a sparkplug or pilot-burner; the second type passes the gases through a catalyst bed which burns the gases at a lower temperature than is possible with the direct-flame burners. Additional equipment in these mufflers is a compressor for air supply and a temperature-actuated bypass to prevent overheating of the device.

A device which replaces the conventional muffler has to fulfill a number of conditions, such as long life and high efficiency of combustion. It should not adversely affect the operation of the engine by creating excessive back pressure, and it should not be a fire hazard. In addition, it should function as an ordinary muffler in eliminating noise. It is difficult to find a suitable place for an afterburner under the car or hood. This may be possible in new cars; for older ones the installation may be a costly engineering job, which adds to the estimated $50-$70 cost of the device. In the many cars with dual exhaust the price has to be doubled.

A partial answer to the price and space problem may be found in accepting less efficient combustion devices. Extensive investigations by automotive engineers have shown that reduction of unburned hydrocarbons and carbon monoxide can be obtained by modification of carburation—for example, by limiting the flow of gasoline during deceleration and by changing spark timing. Also, proper maintenance can reduce exhaust emissions, as has been shown in several motor laboratories. This reduction is of the order of 25 percent but may be as high as 50 percent, depending on the condition of the car.

Control of oxides of nitrogen

At present no control of oxides of nitrogen is contemplated. Several proposals have been made, such as water injection or return of a certain fraction of exhaust air in the intake manifold. Both methods actually work; they rely on a lowering of the flame temperature and consequent reduction in formation of the oxides of nitrogen. A promising approach was recently published whereby the exhaust air is admitted only during acceleration and cruising, when the emission of oxides of nitrogen is highest. Other methods involve enriching the combustion mixture; the excess fuel has then to be burned in an afterburner. There is the possibility that the newer type engines, which initially ignite a rich fuel mixture and subsequently supply the required air, will give a considerable reduction in the formation of the oxides of nitrogen. This is essentially a two-step combustion system, which has been developed and installed on a large scale in the Southern California Edison power plants, yielding close to a 50 percent reduction in the emission of oxides of nitrogen.

The crankcase vent is the second largest point of emission—30 percent of the total. All new cars will be equipped with devices which rely on a closed system in which the gases are led to the air cleaner or to the inlet manifold and are burned together with the normal supply of fuel. Installation is simple and inexpensive (about $5, factory installed). A valve preventing backflow and explosion is the only part which needs inspection or replacement and its cost is readily offset by a slight increase in mileage per gallon.

If the installation cost for used cars can be held within reason and if it is established that there is no extra wear on the engine from the introduction of blowby gases, then there is hope that this type of emission can be eliminated within a few years.

Proposals have been made for control of carburetor and tank losses through drainage of gasoline from the carburetor bowl to a heat-insulated tank. Progress in the control of these losses may have to wait until more accurate knowledge is available on their magnitude at temperatures and driving conditions prevailing in Los Angeles. Preliminary data indicate that on hot days these losses may amount to as much as 100 tons per hour. The release of material such as this may be significant as a contribution to the morning traffic exhaust.

What is being done

Air pollution control is always a balance between a desire to get the cleanest air possible and the price we are willing to pay to reach this goal. Theoretically, any amount of control is possible; in practice this complete control would be prohibitive because the engineering cost rises steeply with higher efficiency. This is true for the control of industry as well as of motor vehicles.

In modern concepts of air pollution control the first consideration is the establishment of acceptable levels of pollution for a community. Attempts can then be made to come as close to these levels as engineering methods and economic factors allow. The adoption of community standards for air quality by the California State Department of Public Health should be hailed as an event of great significance in giving a sound basis for an effective air pollution control program. The Health Department has developed a set of standards for most pollutants indicating adverse, serious, and emergency levels.

The adverse level is one at which eye irritation and plant damage begin to occur and is therefore of great importance to the control effort. An important gauge for Los Angeles smog conditions is the formation of oxidants, consisting largely of ozone produced in the photochemical smog reaction. Oxidants correlate well with symptoms of smog, and many years of observation have established a level of 0.15 parts per million of oxidant above which eye irritation will be noticed by a significant percentage of the population. The level of 0.15 ppm of oxidant was therefore chosen as an “adverse” level and as a basis for control of photo-
chemical smog. It was stipulated that this level should not be reached on more than one percent of the days per year. In order to accomplish this goal for 1970 an 80 percent reduction of hydrocarbon emission would be necessary. In a similar manner the carbon monoxide reduction needed to bring its level down to the state standards has been calculated to require a 60 percent control.

Motor vehicle control

In July 1960 a state law was enacted which calls for such reduction in hydrocarbon and carbon monoxide emission from motor vehicles, and a Motor Vehicle Pollution Control Board was appointed and charged with the responsibility of certifying exhaust emission control devices. Certification of a device requires its operation within the standards calculated by the State Department of Public Health. After certification of at least two devices, a schedule of application of the devices to new and old cars, buses, and trucks was made up with the intention of covering all cars in a period of three years.

A misconception has gradually developed that all we have to do now is to wait for the installations of exhaust control devices and the smog will disappear as scheduled. This is unfortunately not the case. At present there are no exhaust mufflers which will give an 80 percent reduction based on presently available emission data. The application of such devices to a car population would lead to an overall efficiency far short of expectation. Other difficulties arise from the limited life of most devices, which make periodic replacement and inspection necessary. Most experts in the field regard an effective inspection system on the performance of devices as practically impossible. In addition, installation costs on the many makes and models of old cars would be prohibitive.

The smog control calculations are based on the assumption that precursors responsible for various air pollution manifestations are simultaneously reduced by equal percentages. This does not hold true for at least one important participant in the photochemical reactions, the oxides of nitrogen. Their emission is increasing at a rate of 6 to 7 percent per year. These sources are generally of industrial nature and are already partially controlled. In most cases there is no practically feasible engineering method available for significant further control.

Considering these limitations, it is clear that control of emissions of our car population is a long way off if we insist on an 80 percent efficiency. It is therefore expedient to look for somewhat less efficient, less expensive, but more feasible approaches. With the present engineering knowledge in the development of control devices, it should be possible to make rapid progress in a partial control of both new and old cars.

The present motor vehicle pollution control law was a pioneering effort and it was expected that changes in the law would have to be made to cope with the experience gained in its practical application. Changes which should be considered are a revision of standards, which are presently based on concentrations, rather than weight of emission per mile in a prescribed driving cycle. The use of concentration as a standard has distorted the control effort and has diverted attention from the fact that busses, trucks, and large cars contribute far more pollution than economy cars, even though their exhaust concentration may be the same. By considering the weight of emission as criterium, the small car could be readily brought under control with relatively inexpensive means.

As a result of the rigidity of the law, the Motor Vehicle Board has had little opportunity to consider and to take advantage of the opportunities offered by the diversity of use and ownership of motor vehicles, or the uneven distribution of traffic in the basin, and the possibilities of simultaneous control of hydrocarbons and oxides of nitrogen. In a rapidly developing and new field, those responsible for control need a freedom of action to seek and apply the best available method which is the least burden on the community. The control of the car population will cost hundreds of millions of dollars, and the least we can do is to make a thorough analysis of all aspects of smog control to arrive at the best solution of this complicated problem.

Making up the deficiency in control

In accepting a more practical but less efficient control of the car, we have to make up the deficiency in control in some other way. A thorough search should be made on possible further control of stationary sources, and serious consideration should be given to the control of oxides of nitrogen. It is obvious that further gains can be made by use of public transportation, economy cars, better flow of traffic, and electric transportation, to name only a few of the many possibilities which reduce the amount of gasoline used. The control which the community can accomplish is unfortunately beset with many difficulties and it is therefore useful to elaborate on some of the advantages of control by means other than engineering control on the motor vehicle itself.

An inspection of the continuous readings of carbon monoxide concentrations at the downtown monitoring station clearly reveals a peak caused by morning traffic. A calculation shows that the carbon monoxide increase corresponds to about 200 tons, representing the emission of about 100,000 cars. This figure agrees quite well with actual counts of the early morning traffic into Los Angeles. The commuter cloud, containing not only carbon monoxide, but also hydrocarbons and oxides of nitrogen, moves slowly towards Pasadena and Burbank. Under the influence of sun-

November, 1962
light, eye-irritating haze and ozone are formed and recordings at different stations reveal a slow movement of the cloud through the San Gabriel and San Fernando Valleys. By evening, the cloud, which is now considerably spread out, is carried by the east wind back to Los Angeles and it then stagnates, most frequently, west and southwest of the city.

In the meantime, the afternoon and evening traffic creates a new cloud of pollutants, but this time there is not enough sunlight to convert hydrocarbons and oxides of nitrogen to the typical daytime smog. This cloud moves slowly, first to the east a few miles and is then blown back west. This cloud, too, stagnates west and southwest of Los Angeles. As time passes and the cloud moves back and forth through the basin, it expands and covers a large area. The nature of the pollutants will be substantially the same as when they were released the previous evening and this cloud is ready for photochemical smog formation in the morning when the sun begins to shine.

One would not expect sharp peaks in pollutant concentration from this expanded, day-old cloud but rather a long-lasting background of carbon monoxide, oxides of nitrogren, and oxidant. In the morning the expanded morning and evening clouds of the previous day move back to Los Angeles, joining with the new traffic cloud on its way to Pasadena and Burbank.

It is this combination of young and old traffic clouds with the extended one from traffic in the rest of the basin, and the older attenuated clouds from previous days, which form the base on which the morning traffic commuter peak rises. On its path through the basin, traffic continues to supply smog ingredients, hydrocarbons, and oxides of nitrogen. Further amounts of oxides of nitrogen are injected into these streams by power plants located at the entrances to the valleys.

The morning commuter cloud raises the average carbon monoxide level in Pasadena from a background of 10 to 15 ppm, a 30 percent increase. Oxides of nitrogen increase by about 15 percent, indicating the contribution from sources other than motor vehicles. By reducing the commuter peak through a public transport system a considerable improvement could be obtained in lowering the peak pollution values. Consequently, less efficient control on motor vehicles would be required for staying below the state health standards.

Temporary control

Clearly, the proposed 80 percent control methods for motor vehicle emissions are still a long way off. We should therefore consider a temporary control at lower levels of efficiency. It would then be possible to obtain significant reduction with less expensive devices which could also cover the old car population. These methods may consist in the use of afterburners which can readily replace the present muffler, or they may involve changes or alterations in engines and combinations of engine and carburetor adjustments leading to improved combustion. Serious consideration should be given to the prevention of hydrocarbon losses from carburetors and tanks.

Surveys conducted in several large cities have shown that a substantial percentage of commuters would switch to public transportation when it is good. The emphasis is on good; that is - frequent, rapid, extensive service, especially in the sprawling cities of the Los Angeles basin. There must be some radical changes in our ways of thinking about how this transportation should be organized and financed. We must get away from the idea that this is a direct profit-making business, and accept it as a public service paid in part by taxation.

A better flow of traffic in cities and on our freeway system contributes to air pollution control by eliminating the frequent idling, acceleration, and deceleration typical of stop-and-go traffic.

It should be clear to anyone that a car running 30 miles to the gallon produces less pollution than one which gets only 15. The concentration may be the same in both cases, but the exhaust volume -- and therefore the total weight and emission -- is considerably less than that of a bigger car. Perhaps some public-spirited individuals may consider this an additional reason for buying a small car, especially for town driving.

Proper maintenance of cars

In the same category of voluntary contributions is proper maintenance of cars. A survey has shown that 40 to 50 percent improvement in exhaust emission can be accomplished. It does not seem unreasonable to ask the individual motor vehicle owner to give his equipment the same care that industry is forced to give by law. The enforcement of such an approach may well be impractical; nevertheless, those who complain of smog would at least have their cars in proper shape. Since about 80 percent of the people don't like smog, this should make a considerable reduction.

It has become quite clear that controlling smog in Los Angeles is not just a matter of attaching a gadget to our cars. The problem is directly connected with the growth of our cities, and planning is necessary for an orderly expansion. Air pollution plays a vital part in this expansion, and a really effective control program must include efforts by the local community in addition to the engineering control of industry and motor vehicles.

The time has come for a critical appraisal of the smog situation and the development of a plan of action that takes into consideration technical, social, and economic factors. Such a plan, when actively supported by all levels of government, and backed by the community, can lead to clean air in Los Angeles.

Engineering and Science