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The importance of automobile exhaust as a source of atmospheric pollutants has been recognized for several years. With the control of stationary sources in geographic areas such as Los Angeles County, the automobile has become the major uncontrolled source of air pollution.

The three major pollutants emitted by automobiles are unburned hydrocarbons, carbon monoxide, and oxides of nitrogen. Seventy percent of the emissions are from the exhaust. Maximum emission standards of 275 ppm hydrocarbons as n-hexane and 1.5 mole percent carbon monoxide in automotive exhaust have been enacted in California. Control measures for the oxides of nitrogen may possibly be effective for 1970 model vehicles.

Exhaust control devices for hydrocarbon and carbon monoxide

emissions submitted to the California Motor Vehicle Pollution Control Board for approval have included catalytic converters, direct-flame afterburners, engine modification systems, and secondary air injection at the exhaust port systems. Three of the automobile manufactures may use the fourth system which involves introduction of secondary air into the engine exhaust ports to promote flameless oxidation of hydrocarbons and carbon monoxide to carbon dioxide and water. Since this control system introduces air to the high temperature exhaust gases at the exhaust port, the question arises whether oxides of nitrogen might be formed. This would be detrimental from the outlook that oxides of nitrogen must be controlled.

The purpose of this work was to determine the effects on the emissions of oxides of nitrogen from a gasoline engine by the installation and operation of an exhaust port secondary air injection system. The engine under test, given to Oregon State University by the Ford Motor Company, was installed in a vehicle and operated on a chassis dynamometer.

Measurements of oxides of nitrogen emissions with and without the air injection system in operation were made both during steady state and transient conditions. For transient measurements, the vehicle was operated on the California seven-mode test cycle. Oxides of nitrogen samples were taken by a progressive grab sampling technique and analyzed with an absorption spectrophotometer built at Oregon State University. Further measurements included unburned hydrocarbon, carbon monoxide, and carbon dioxide analyses with commercial non-dispersive infrared analyzers and total carbon measurement with a commercial hydrogen flame ionization analyzer. These analyses were made for the purpose of determining air dilution factors and correlating data with other work being done in the field.

The results of the investigation are summarized as follows:

1) The addition of secondary air at the exhaust ports increased the oxides of nitrogen emissions during acceleration for both rich and lean mixture operation. As high as 40 percent increase occurred during operation with the rich carburetor. Appreciable increase also occurred during high speed steady state cruise conditions with the rich carburetor. Weighted average concentrations of NO_x for operation on the California cycle were not determined.

2) The grab sampling and spectrophotometric analysis methods for the oxides of nitrogen worked well during the testing. However, the time required to take a grab sample, three seconds, was too long to obtain instantaneous analysis. Sampling probes should be located closer to the engine to avoid mixing of exhaust from separate modes in the exhaust pipe prior to analysis. 3) Temperatures in the exhaust manifold were not markedly changed by the injection of secondary air into the exhaust ports. However, temperatures were 50 to 100° F higher at the end of the tailpipe due to increased exhaust mass flow rate.

4) The vehicle with the air system installed met California standards for operation with the rich carburetor, but emitted a higher concentration of unburned hydrocarbons than the standard during operation with the lean carburetor.

THE EFFECT OF AIR INJECTION AT THE EXHAUST PORTS OF A GASOLINE ENGINE ON THE OXIDES OF NITROGEN EMISSIONS

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THE EFFECT OF AIR INJECTION AT THE EXHAUST PORTS OF A GASOLINE ENGINE ON THE OXIDES OF NITROGEN EMISSIONS

I. INTRODUCTION

The Problem

The importance of automobile exhaust as a source of atmospheric pollutants has been recognized for several years. The concentration of automobiles and other sources of air pollutants presents the problem of a polluted sea of air in which the inhabitants must live. It is estimated that 90 percent of the urban population of the United States now live in areas which have air pollution problems. This includes a total of nearly 6000 communities (14, p. 25).

Although air pollution is certainly not peculiar to the area, California and Los Angeles County in particular are the most well known areas of air pollution in the United States. The problem in Los Angeles County has stemmed from unusual meteorology, abundant sunshine, and a large number of sources of air pollution.

The pollution problem in California as well as most other highly populated areas is caused by pollutants known as smog. Smog is not the combination of smoke and fog as the name implies, but the result of photochemical reactions between pollutants in the atmosphere (14, p. 27). In Los Angeles County, smog is evident two-thirds of the year through its effects of eye irritation, bleachlike odors, plant damage, and a decrease in visibility due to a brownish haze (14, p. 26).

The basic ingredients necessary for the photochemical production of smog are hydrocarbons, oxides of nitrogen, and the ultraviolet rays of the sun. The reactions occurring are basically as follows (12, p. 342):

> $NO_2 + hv \rightarrow NO_2^*$ $NO_2^* \rightarrow NO + O$ $O + O_2 \rightarrow O_3$ $O_3 + hydrocarbons \rightarrow organic complexes$ hv = quantum of light* = excited state

The nitric oxide produced oxidizes to nitrogen dioxide during the night, completing the smog cycle. Topography and meteorological conditions are instrumental in the formation of temperature inversions, which trap the photochemical smog, holding it within a definite area such as the Los Angeles basin. This allows the pollutant concentration levels to build up to a point of affecting the life of the inhabitants.

To combat the air pollution problem in California and other sections of the United States, air pollution control districts (APCD) have been formed. The Los Angeles County APCD, formed in 1948, has brought stationary sources of air pollutants well under control (31, p. 80; 25, p. 1). Although there was an improvement in visibility, the effects of eye irritation and plant damage remained (14, p. 26). As an example of the problem which still exists, information released by the Los Angeles County APCD in January 1963 gives daily emissions of the three most important primary pollutants (31, p. 8).

Hydrocarbons - 2235 tons per day, 73 percent of this from gasoline-powered vehicles.

Carbon monoxide - 8580 tons per day, 96 percent from motor vehicles.

Nitrogen oxides - 850 tons per day, 57 percent from motor vehicles.

With the control of stationary sources, the automobile has now become the major uncontrolled source of air pollution in Los Angeles County.

At the present time there are 3,250,000 gasoline-powered motor vehicles in Los Angeles County, and nine million in the state of California. The statewide total is expected to increase to 11 million by 1967, 12.7 million by 1970, and 16 million by 1980 (13, p. 444; 31, p. 80).

Pollutants are emitted from three sources on the automobile: engine exhaust, crankcase blow-by, and fuel evaporation. Seventy percent of the total emissions are from the exhaust gases and 24 percent from the crankcase blow-by gases (9, p. 27).

In 1960 the Motor Vehicle Pollution Control Board (MVPCB) was formed in California with its major objective to control pollutant emissions from mobile sources (31, p. 80). The board accepted emission standards set forth by the California Board of Public Health. The standards include concentration limits for both automotive engine exhaust and crankcase emissions. The standards for the automotive exhaust system are hydrocarbons not to exceed 275 ppm by volume as normal hexane and a maximum of 1.5 mole percent of carbon monoxide. The above concentrations are to be measured over a specified driving cycle (15, p. 4). Other specifications were set forth which must be considered when designing control devices for automotive exhaust: (1) system must meet emission standards for at least 12,000 miles, (2) system must have acceptable back pressure, (3) system must satisfy specified heat and noise levels, (4) system must have mechanical reliability, (5) system must be of reasonable cost to the motorist (31, p. 82).

With the large increase in the number of vehicles estimated, any decrease in the pollutant concentrations will soon be nullified by the vehicle increase. Therefore, a progressive program for the reduction of existing standards and enactment of standards for other constituents such as the oxides of nitrogen will be necessary. Realizing this, the California Board of Health has announced more strict control restrictions on automobile exhaust for 1970. Hydrocarbon emission standards will be reduced to 180 ppm by volume; a reduction in the carbon monoxide standard is also predicted (4, p. 7). The Board is aware that oxides of nitrogen emissions must also be reduced.

> Although no standards have yet been set for oxides of nitrogen, their control will be a reality in the near future. The State Board of Public Health gave ample notice in October that it intends to act on this objectionable emission from motor vehicles. Control measures may possibly be effective for 1970 model vehicles (4, p. 7)

Crankcase emissions represented the lesser problem to control. The crankcase emission standards have been met by the installation of recirculation devices on the engine. By the end of 1965, 85 percent of the automobiles in California will have crankcase control devices (31, p. 83).

Control of the exhaust gas emissions however, has been a more difficult problem. Average values for the emissions of uncontrolled automobile exhaust are carbon monoxide, 3 to 3.5 percent; unburned hydrocarbons, 800 to 950 ppm; and oxides of nitrogen, 900 to 1100 ppm (19, p. 327). Thus an 80 percent reduction in the carbon monoxide and hydrocarbon emissions is required. The major problem in controlling automobile exhaust is that the concentrations of the different pollutants vary considerably under various driving conditions. The flow of exhaust gases is also by no means constant. The design, construction, and certification of exhaust control devices has taken several years to complete.

Control devices which have been submitted for approval may be categorized generally as (1) catalytic converters, (2) direct-flame afterburners, (3) engine modification systems, and (4) exhaust port secondary air injection systems (31, p.82; 30, p. 44). By September of 1964, three catalytic converters and one direct-flame afterburner had been approved by the Motor Vehicle Pollution Control Board for installation on new cars. This led to the requirement that exhaust control devices must be installed on all 1966 model cars sold in California.

The approved control devices had been designed by private companies to be sold to the automobile manufacturers. But, the automobile manufacturers announced that they would equip the 1966 model automobiles sold in California with devices of their own design (30, p. 44).

Chrysler Corporation has designated the system which it intends to use as the "Cleaner Air Package." This system aims to reduce the pollutants by having the engine burn the fuel more completely in the cylinder. This is being accomplished with lean carburetion and an altered distributor used to advance the spark during deceleration (31, p. 85). The other three automobile manufacturers may use a control system which involves the introduction of air into the exhaust ports of the engine to promote flameless oxidation of hydrocarbons and carbon monoxide to carbon dioxide and water (7, p. 1).

At the same time as control methods were being developed for hydrocarbons and carbon monoxide, it was realized that the increasing concentrations of the oxides of nitrogen in the atmosphere were a potential health menace. This was officially recognized by Los Angeles County in 1955 when the oxides of nitrogen were included in the alert system (25, p. 1). The oxides of nitrogen include eight to ten distinct species. However, it has been shown by equilibrium considerations that nitric oxide (NO) and nitrogen dioxide (NO₂) are the only two important as air pollutants (35, p. 733). Data reported on the oxides of nitrogen is usually for the sum of the oxides, known as NO₂.

The primary and almost sole source of NO_x in the atmosphere is the combustion of fuels. The high NO_x content of urban atmospheres is produced 65 to 85 percent from burning gasoline in automobiles and 15 to 35 percent from gas and fuel burning (12, p. 343).

To eliminate or alleviate the annoying manifestations of Los Angeles smog, these emissions (NO_x) probably must be curtailed (12, p. 343).

Concern with the oxides of nitrogen in air pollution stems from (23, p. l):

- 1. Oxides of nitrogen participate in the photochemical reaction that produces eye and respiratory irritatation, damage to vegetation, visibility reduction, and ozone.
- 2. NO₂ attenuates sunlight so that in the presence of a sufficient amount of this compound, the atmosphere becomes reddish-brown in color.
- 3. NO₂ is a toxic substance that has direct effects on health. It also has indirect effects on health through the secondary pollutants produced in the photo-chemical reaction.

The control of the oxides of nitrogen emissions from automobiles is one of the next steps in the emission controls on automobiles.

Since the control systems which employ secondary air injection introduce air to the high temperature exhaust gases at the exhaust port, the question arises whether during the process of reduction of hydrocarbons and carbon monoxide, are oxides of nitrogen being formed? This would be detrimental from the outlook that oxides of nitrogen must be controlled. The answer to this question is the purpose of this work.

Scope of Study

The purpose of this work was to determine the effects on the emissions of oxides of nitrogen from a gasoline engine by the installation and operation of an exhaust port secondary air injection system. The engine under test, given to Oregon State University by the Ford Motor Company, was installed in a vehicle and operated on a chassis dynamometer.

Measurements of oxides of nitrogen emissions with and without the air injection system in operation were made both during steady state and transient conditions. For transient measurements, the vehicle was operated on the California Seven-Mode Test Cycle. Oxides of nitrogen samples were taken by a progressive grab sampling technique and analyzed with an absorption spectrophotometer built at Oregon State University. Further measurements included unburned hydrocarbon, carbon monoxide, and carbon dioxide analyses with commercial non-dispersive infrared analyzers and total carbon measurement with a commercial hydrogen flame ionization analyzer. These analyses were made for the purpose of determining air dilution factors and correlating data with other work being done in the field.

The entire project was carried out by one graduate student under the supervision of two professors. The work was financially supported by the Public Health Service Division of Air Pollution.

II. THEORY

The term "oxides of nitrogen" includes a number of combinations of oxygen and nitrogen. Certain conditions, i.e., temperature and pressure, favor the formation or existance of one combination or another. The more stable oxides of nitrogen include: N_2O , nitrogen oxide; NO, nitric oxide; N_2O_3 , nitrogen trioxide; NO_2 , nitrogen dioxide; N_2O_4 , nitrogen tetroxide; and N_2O_5 , nitrogen pentoxide (9, p. 1).

The oxides of nitrogen are formed by the combination of oxygen and nitrogen at high temperatures. A commercial process for the production of nitric oxide heats air to a sufficiently high temperature to allow the oxygen and nitrogen to combine to a limited extent. At 3800° F, one to two percent NO is obtained (9, p. 2). It is also necessary, however, that the oxides of nitrogen mixture be cooled at a rapid rate to prevent decomposition (10, p. 1719).

The combustion process of an internal combustion engine satisfies both of the above requirements for the formation of oxides of nitrogen. Peak cycle temperatures as high as 5000° R can occur during the process (32, p. 48). Any excess oxygen in the combustion chamber could combine with the nitrogen under the combustion conditions. Rapid cooling of the exhaust gases occurs during exhaust expansion and blowdown which drops the temperature of the oxides of nitrogen to a point where the decomposition to oxygen and nitrogen is extremely slow due to small reaction rates (34, p. 3).

Although all of the above mentioned oxides of nitrogen may be present in very small amounts, equilibrium determinations show that nitric oxide is the only oxide which will be formed to any extent at combustion temperatures (35, p. 734). The concentrations of NO in automotive exhaust gas are a function of peak cyclic temperature, pressure, and air-fuel ratio. An increase in combustion temperature or pressure will produce an increase in the exhaust concentrations of NO (35, p. 737). Lean air-fuel ratios, greater than 15 to 1, produce more NO than do rich mixtures. Bishop and Nebel show the maximum oxides of nitrogen concentrations to occur at an air-fuel ratio of 17 to 1 (2, p. 511).

Once the nitric oxide reaches the atmosphere, oxidation to NO₂ begins. This reaction is of the third order, occurring more quickly at low temperatures (11, p. 2372). This reaction produces the NO₂ which is necessary to initiate the smog cycle.

The air injection system installed to reduce the emissions of unburned hydrocarbons and carbon monoxide by flameless oxidation, introduces the secondary air to the exhaust stream at the exhaust port. Whether oxides of nitrogen might be formed by this system depends on equilibrium constants and kinetic reaction rates at exhaust gas temperatures. Exhaust gas temperatures may be as high as 3000° F at the exhaust valve (33, p. 198). The product gases remain in the exhaust system for approximately one second, decreasing in temperature to nearly 200° F at the end of the tailpipe. Temperatures as high as 1300° F were found by thermocouple measurement in the exhaust manifold during this study.

A consideration of the equilibrium concentrations of NO and NO_2 which could be formed in the exhaust manifold is included in Appendix A. Assuming the equilibrium temperature to be 1300° F, the results indicate that the concentration of NO_x that could be formed due to the addition of the secondary air to the exhaust gases is about ten ppm. However, at the 1300° F temperature assumed, the reaction rate would not be large enough to produce even this small concentration of NO_x (9, p. 10).

It should be cautioned that in this attempt to predict possible concentrations of oxides of nitrogen produced from secondary air injection, many assumptions as to operating conditions were made, i.e., exhaust temperature, air-fuel ratio, etc. It has been shown that the concentration of NO in equilibrium with nitrogen and oxygen increases with temperature and oxygen concentration (10, p. 1720). From data presented by Daniels and Gilbert (10, p. 1721), under conditions of 3100° F, 80 percent nitrogen, and 10 percent oxygen, the equilibrium concentration of NO_x would be 5700 ppm and the reaction rate 1575 ppm per second.

The question then remains, does the air reach a high enough temperature and remain there for a long enough period of time for significant amounts of oxides of nitrogen to be formed?

III. APPARATUS

An overall view of the general layout with the principle apparatus used in the experimental work is shown in Figure 1. As shown, the work was carried out with a vehicle installed on a chassis dynamometer in a Quonset hut at Oregon State University. An electrically driven centrifugal fan used for cooling was located at the front of the vehicle. Along the right side were located the temperature recorder, the oxides of nitrogen sampling train, and the non-dispersive infrared analyzers. The NO_x spectrophotometer equipment is evident at the right corner of the picture. The hydrogen flame ionization analyzer was located to the left rear of the vehicle.

The apparatus has been categorized into the following groups: (1) air injection system, (2) engine and vehicle, (3) dynamometer, (4) exhaust and sampling system, (5) gas analysis equipment.

Air Injection System

The secondary air injection system consists of an air pump, rubber air hoses, and a manifold. The air for the system is supplied by a diaphragm pump operated by a belt from the engine fan pulley. Since the air flow for maximum hydrocarbon reduction is generally less than that for maximum reduction of carbon monoxide, the pump was designed to provide an air flow which was a



Figure 1. Overall test layout.

compromise between the two (3, p. 7). The volume flow characteristics of the pump are included in Appendix D. The air injected to the exhaust is a function of the engine speed and the back pressure to the pump.

The injection air is obtained directly from the engine compartment and discharged by the pump to the rubber hoses. The 5/8 inch I. D. air hoses deliver the air to the secondary air manifolds, one on each side of the engine. The air is distributed through a 7/8 diameter manifold to 5/16 inch O. D. tubes leading to each exhaust port. The air is introduced to the exhaust gases within 1/2 inch of the exhaust valve. With this system, secondary air is delivered to the exhaust ports continuously, not just during the exhaust stroke as has been attempted in development phases (7, p. 15).

Figure 2 shows the secondary air system mounted on the test engine. The air pump is located on the front of the engine with the intake port on the left side. One of the air hoses crosses the engine in front of the carburetor, connecting to the secondary air manifold below the rocker-arm cover. The secondary air manifold, mounted parallel with and above the exhaust manifold, is connected to the delivery tubes with heat resistant rubber tubing.

The system tested here, although of the same general design, is not an exact duplicate of any of the systems which may be used by the automobile manufacturers. A large development program was



Figure 2. Secondary air injection system mounted on test engine.

necessary to find an air pump which would satisfy the requirements of the system. The pump to be used by the manufacturers will be a semi-articulated vane pump (6, p. 18). Other than the pump and possibly a few production refinements, the manufactured systems will be the same as the system tested during this study.

Engine and Vehicle

The engine used in this work was removed from the assembly line, dismantled and inspected, and reassembled by the Ford Motor Company. The secondary air system was installed at that time. The completed unit was then shipped to Oregon State University.

The engine used was a 1965 Mercury V8, with 390 cubic inches of piston displacement, a 9.4 compression ratio, and rated at 250 bhp at 4400 rpm and 378 pound feet of torque at 2400 rpm. The standard carburetor for the engine was a Ford two-throat type. The engine was also supplied with two additional two-throat carburetors, each having been calibrated and set on a carburetor test stand. One carburetor was set for rich limit operation and the other to lean limit.

The engine was installed in a 1965 Ford Galaxie 500 obtained by an agreement with the Ford Motor Company for use in this work. The car was equipped with the Cruise-O-Matic three speed automatic transmission, an axle ratio of 3 to 1, and 15 inch wheels. The weight of the vehicle with the test engine installed was 3865 pounds.

Dynamometer

The test vehicle was operated on a Clayton Model C-41 chassis dynamometer. The dynamometer utilizes two seven inch diameter rolls for operation, and a hydraulic power absorption unit. The amount of power absorbed is controlled by the operation of electrically operated solenoid valves to add or remove water from the system (8, p. 6).

The dynamometer is equipped with a 4000 pound equivalent inertia flywheel to simulate vehicle inertia during acceleration and deceleration. The complete unit is mounted flush with the floor.

Exhaust and Sampling Systems

A schematic drawing of the exhaust and sampling systems used during this study is shown in Figure 3. To measure total exhaust flow and to take representative samples of the exhaust of all cylinders of the engine, the dual exhaust system on the test car was joined behind the mufflers into a single pipe. To maintain the normal exhaust back pressure on the engine, the cross-sectional area of the single pipe was made twice that of the exhaust pipes replaced. The single exhaust pipe with sampling probes installed is shown in Figure 4.

Sample Explanation





Figure 3. Schematic of Exhaust and Sampling System.



Figure 4. Exhaust pipe with gas sampling probes installed.

Bare-wire chromel-alumel thermocouples were installed in the exhaust manifold at points T_1 and T_2 shown in Figure 3 and in the exhaust pipe at point T_3 to measure exhaust gas temperatures. Thermocouple (1) was installed in the exhaust manifold three to four inches from one exhaust valve to measure the temperature of the exhaust gas from one cylinder. Thermocouple (2) was installed at the exhaust manifold flange, where the exhaust pipe joins the manifold, to measure the temperature of the exhaust from four cylinders combined. Thermocouple (3) was installed near the end of the exhaust pipe to measure the exhaust gas temperature leaving the pipe.

Bare-wire thermocouples were used to obtain quick response to temperature changes. The fast response of the bare-wire thermocouples was necessary to measure maximum temperatures during transient operation. Thermocouple (1) was replaced during steady state testing with a shielded chromel-alumel thermocouple in an attempt to obtain a correction factor for radiation losses of the barewire thermocouples. Thermocouple outputs were recorded with a Brown Electronik chart recorder.

Gas sampling probes were installed as indicated in Figure 3 at points S_1 , S_2 , and S_3 . The probes were 1/4 inch thick-walled stainless steel tubing. The end of the tube was brazed closed and sampling ports, 3/64 inch diameter, were drilled in a spiral pattern along the tubing for a distance of one foot from the closed end. The probes were installed parallel with the exhaust flow, making a right angle and leaving the pipe as shown in Figure 4. The probes extended forward one foot from the point of entrance to the exhaust pipe. Each probe was staggered within the diameter of the pipe so as to provide the least amount of interference to the probes downstream. The first gas sampling probe led to the flame ionization analyzer, the second to the non-dispersive infrared analyzers, and the third to the oxides of nitrogen sampling train.

A Pitot tube was installed in the end of the tailpipe, shown as S_4 in Figure 3. The Pitot tube was included to determine exhaust gas flow rates during steady state conditions. The pressure difference was measured with an Ellison inclined draft gage manometer.

Gas Analysis Equipment

The oxides of nitrogen concentrations in the exhaust gas were determined by measurement with an absorption spectrophotometer. The analytical technique was developed, and an instrument constructed, by Nicksic and Harkins (28, p. 985). The instrument used during this test was built at Oregon State University in 1962 by Douglas E. Johnson (20, p. 6-42). Improvements were made on the original equipment by Donald J. Addicott in 1964 (1, p. 7-17).

The spectrophotometer utilizes a tungsten filament light source and a light filter to produce light in the frequency range of 3900 Angstroms. The light is projected through a 12 inch long, 154 cubic centimeter, stainless steel sample tube to a photocell on the other end. Nitrogen dioxide in the sample cell absorbs light in the range of 3900 Angstroms, reducing the amount of light incident upon the photocell. The photocell current, which is a function of the intensity of light incident upon the photocell, is passed through a large resistor. The voltage drop across the resistor is amplified by a Beckman pH meter and recorded on a Bausch and Lomb Model VOM-5 Recorder. The recorder deflection is proportional to the nitrogen dioxide concentration in the sample cell.

Calibration equipment for the spectrophotometer included a bottle of high purity nitric oxide, a bottle of nitrogen, two-liter flasks, and calibrated syringes. The analyzer and calibration equipment layout is shown in Figure 5.

The sampling train used for obtaining NO_x samples, shown in Figure 6, consisted of the sample probe, a copper coil immersed in an ice bath to condense water vapor from the sample, a U-tube containing Drierite to further dry the sample, and a Gelman Model 13152 vacuum pump to pull the sample gas through the apparatus. Sample train flow rate, measured by a rotameter, was held constant. The NO_x samples were taken with a 100 cubic centimeter syringe by inserting a hypodermic needle into the rubber tubing.

Continuous measurement of the exhaust gas concentrations of



Figure 5. NO_x spectrophotometer and calibration apparatus.



Figure 6. NO_x sampling train.
unburned hydrocarbons, carbon monoxide, and carbon dioxide were made with three Beckman Model IR-15A Non-dispersive Infrared Analyzers, (NDIR). The analyzers, including recorders and calibration gas bottles, were mounted on a portable console by Gary D. Jaros and Neill R. Parkin in 1964 (18, p. 15-16). The analyzers are the standard specified for use by the California Motor Vehicle Pollution Control Board for the determination of system effectiveness over the California driving cycle. The portable analyzer console is shown in Figure 7.

The gas sample was pulled through a water-cooled condenser and a paper filter prior to introduction into the detectors. The three detectors measure the constituent concentrations by the amount of infrared light absorbed by the gas flowing through a sample cell. Texas Instrument Recti-riter Recorders continuously recorded the output of the three analyzers.

Two sample cells were used with the hydrocarbon analyzer, both sensitized to normal hexane. For testing over the California driving cycle without the secondary air system in operation, a 5.25 inch sample cell was used to give a detection range to 10,000 ppm. For all other testing, a 13.5 inch sample cell was used, calibrated to 2900 ppm at full scale deflection of the recorder. A one and onehalf inch wet CO₂ filter cell was installed in both cases.

The carbon monoxide analyzer utilized a 1/8 inch sample cell.



Figure 7. Non-dispersive infrared analyzer portable console.

This analyzer was calibrated for 9.4 percent CO at 90 percent deflection of the recorder.

The carbon dioxide analyzer utilized a 1/8 inch sample cell. The analyzer was calibrated for 14.5 percent CO₂ at 90 percent deflection of the recorder.

The measurement of unburned hydrocarbons with a NDIR analyzer sensitized to normal hexane is deficient in that the response is quite dependent on hydrocarbon type (17, p. 592).

> In contrast, the flame-ionization type of hydrocarbon detector can be made to respond essentially uniformly to all hydrocarbons (17, p. 592).

For purposes of a carbon balance, to be explained later, a measurement of total unburned hydrocarbons was desired. A Beckman Flame Ionization Detector was used to measure total unburned hydrocarbons in the exhaust stream.

The flame ionization detector consists of a regulated fuel, air, and sample delivery system, an internal burner, electronics for measuring the ion current, and a diaphragm vacuum pump. Hydrogen and air are delivered to the burner where a flame is maintained. The flame of pure hydrogen contains a negligible number of ions, but the addition of even traces of hydrocarbons produces a large amount of ionization. The ions are accelerated to a collector electrode by an electric field set up between the burner jet and the electrode. The generated ion current is proportional to the rate of introduction of hydrocarbon molecules into the flame (26, p. 467-469).

To reduce contamination of the instrument, the gas sample was pulled through a water-cooled condenser and a paper filter. The output of the detector was continuously recorded with a Bausch and Lomb Model VOM-7 Recorder. The analyzer, recorder, fuel and air gas bottles and sample train were mounted on a portable cart shown in Figure 8.



Figure 8. Flame ionization detector mounted on a portable cart.

IV. PROCEDURE

Preliminary Operations

Prior to the beginning of testing, it was necessary to accomplish certain preliminary operations. These included programming the vehicle to the California seven-mode driving cycle, setting the dynamometer for road load, and instrument calibration.

For portions of the testing, the vehicle was operated on the California seven-mode driving cycle. A description of the California cycle is included in Appendix D. The cycle was strictly adhered to except for the following:

Due to the characteristics of the chassis dynamometer, a constant deceleration during the seventh mode was not possible.
The rate of deceleration at closed throttle from 50 mph was too great for the first portion of the mode, but decreased allowing the overall deceleration from 50 to 20 mph to occur during the specified time period. A plot of speed versus time is included in Appendix D.

2) The cycles were run with the engine at normal operating temperature. No attempt was made to run warm-up cycles.

It was originally planned to program the vehicle to automatically follow the California cycle. The engine control device constructed by Jaros and Parkin (18, p. 10) was intended to be used. However, large differences in engine operating variables from those for which it was originally designed and a lack of sufficient time to modify the device prevented its use for cycling the vehicle. The device did prove useful later, however, to hold the engine at constant throttle for steady state testing.

A driver was used to operate the test vehicle through the California cycle. Vehicle speed versus time instructions were recorded on a tape recorder. The vehicle driver, equipped with a headset, followed the instructions played to him from the tape recorder. A system was constructed which allowed the driver to mark pips on the recorders at the beginning of each cycle. Once the driver was familiar with the operation, the cycle could be driven within one mile per hour of the speed and one second of the time requirements, except as explained in (1) above.

As specified by the instructions for the California test procedure (5, pt. 1, p. 5), the dynamometer was set to impose road load on the test vehicle at 50 mph. Prior to installation on the dynamometer, the vehicle was operated on level road at 50 mph to determine the engine manifold vacuum during these conditions. The load on the dynamometer was adjusted until the vehicle operated at 50 mph with the same manifold vacuum. The fact that this does not give the proper road load at lower speeds is recognized by the California MVPCB (5, pt. 1, p. 9). Instrument calibration and the construction of calibration curves was necessary prior to testing operations. The Beckman Model 15A NDIR analyzers were calibrated with gas mixtures containing known concentrations of normal hexane, CO and CO₂. Details of the calibration gases and the resulting calibration curves are included in Appendix C.

The hydrocarbon analyzer was calibrated for both the 5.25 inch and the 13.5 inch sample cells. With the 5.25 inch cell installed, the instrument was adjusted to read 2900 ppm as n-hexane at 30 percent of full scale deflection of the recorder. With the 13.5 inch cell installed, the analyzer was adjusted to read 2900 ppm as n-hexane at full scale deflection of the recorder.

The CO analyzer was calibrated to 9.4 percent carbon monoxide at 90 percent full scale deflection of the recorder.

The CO_2 analyzer was calibrated to 14.5 percent carbon dioxide at 90 percent full scale deflection of the recorder.

The Beckman hydrogen flame ionization analyzer was calibrated with one of the gases used for NDIR calibration. Details of the calibration and calibration curves for the ranges used during testing are included in Appendix C.

To calibrate the NO_x spectrophotometer, it was necessary to construct a small gas blending apparatus. The apparatus included two, two-liter flasks, a mercury manometer, a vacuum pump, nitrogen and nitric oxide gas bottles, and syringes. The calibration gases were blended in the following manner. The two-liter flasks were evacuated to 29.5 inches of mercury vacuum and purged with nitrogen to remove any traces of NO. Both flasks were then partially filled with nitrogen, one closed off, and the other filled with nitrogen to atmospheric pressure. A specific amount of NO was transferred from the gas bottle to the partially filled two-liter flask in a syringe. The NO was injected through a serum stopper in one end of the flask. By rotating the stopcock on the flask quickly and always keeping the pressure in the other flask higher, the blending flask was filled to atmospheric pressure with nitrogen without allowing any of the NO to escape. A sample calculation of NO concentration is included in Appendix C.

The analyzer was then prepared for introduction of the sample by evacuating the sample cell several times and purging with oxygen. The cell was then evacuated to 29.5 inches of Hg vacuum and increased to 4.5 inches Hg absolute with oxygen. A 100 cubic centimeter sample was removed from the two-liter flask in a syringe and injected into the sample cell through a serum stopper. The sample cell was then brought to atmospheric pressure with oxygen.

The NO in the presence of the excess oxygen readily oxidized to NO_2 , observed by a deflection on the recorder. Fifteen to twenty minutes were necessary to complete the conversion to NO_2 , indicated by a steady recorder trace. When the analysis was completed, the cell was evacuated and purged in preparation for the next analysis. The instrument was calibrated for three ranges: 0-1000 ppm, 0-1600 ppm, and 0-3000 ppm. Calibration curves are included in Appendix C.

Testing Operations

The testing was accomplished in two parts: constant speed steady state operation and California seven-mode cycle operation. Tests were run using the rich and lean limit carburetors supplied with the engine, with and without the secondary air injection system in operation. In all six cases, test periods were about 12 hours in duration.

The engine was started and allowed to warm-up for one hour prior to the beginning of each test period. During this time period, the vehicle was stabilized at 50 mph for a short time to adjust the dynamometer to the proper setting for road load.

The NDIR analyzers were turned on and allowed to stabilize during the engine warm-up period. The instruments were set by flowing the up-scale calibration gas and nitrogen for zero reading through the system. The instrument calibration was checked several times during each test period.

The hydrogen flame ionization detector was turned on and

allowed to warm-up during this period. The instrument was zeroed by drawing air through the sample system. For the range in which the instrument was operated, the hydrocarbon concentration in the air did not affect the zeroing of the instrument.

The filament and photocell in the NO_x spectrophotometer were turned on and allowed to stabilize. Other portions of the system were left on continuously to avoid instrument drift. The system was evacuated and purged with oxygen in preparation for the first sample.

Other preliminary operations included filling the condenser ice bath of the NO_x sampling train, turning on the cooling water for the NDIR and flame ionization analyzer condensers, and turning on the dynamometer cooling water. The delay time from the engine to the exhaust analyzers was checked each day. The time required for an abrupt change to be measured by the hydrocarbon analyzers due to a quick throttle closure was measured with a stop watch. The time delay to the NO_x sampling point was determined by connecting the NDIR instruments to the end of the NO_x sampling train.

The testing schedule which was followed is shown in Table 1. Other tests such as determinations of air pump flow characteristics and thermocouple corrections were run separately from the above tests.

The first series of tests was run with the rich limit carburetor installed on the engine. For the first test period, the vehicle Table 1. Sequence of testing.

Test No.	Description						
1	Rich Limit Carburetor, Steady State, with and without air system						
2	Rich Limit Carburetor, California Cycle, without air system						
3	Rich Limit Carburetor, California Cycle, with air system						
4	Lean Limit Carburetor, Steady State, with and without air system						
5	Lean Limit Carburetor, California Cycle, without air system						
6	Lean Limit Carburetor, California Cycle, with air system						

was operated at steady state conditions of 10, 20, 30, 40, and 50 mph. A general description of the actual testing procedure is discussed below.

Once the preliminary operations had been completed, the vehicle, without the secondary air system in operation, was set at a specified speed by holding the throttle control against a stop. The vehicle required 10 to 15 minutes to reach steady state conditions. The NO_x sampling train was connected to the sample probe and the vacuum pump turned on. The sample was removed from the rubber tubing by a 100 cubic centimeter syringe. The time required to pull the sample through the large hypodermic needle was found to be

three seconds. To assure that the sample was 100 cubic centimeters at atmospheric pressure, a slightly larger amount was drawn into the syringe and the syringe stopcock closed. The stopcock was reopened, allowing the excess to slowly bleed out of the hypodermic needle until 100 cubic centimeters remained. The syringe plunger was kept under slight pressure during the removal of the excess sample to allow no chance for sample contamination by air. The sample was carried to the NO_x analyzer and injected into the sample cell. The same steps were carried out for analysis as had been during calibration.

During the time required for analysis of the NO_x sample, 15 to 20 minutes, two samples were taken with the NDIR analyzers, one sample with the flame ionization detector, and temperatures were recorded from the three thermocouples. Care was taken with all instruments that flow rates were the same as during calibration. A Pitot tube traverse was made at the end of the tailpipe during each test.

When the recorder deflection on the NO_x analyzer had stabilized, the sample cell was evacuated and purged with oxygen in preparation for the next sample. A second NO_x sample was taken and analyzed in the same manner.

During the analysis of the second NO_x sample, the secondary air system was placed into operation by connecting the air hose to the outlet of the air pump. Once steady state conditions were attained, sampling operations described above were repeated. Thus, steady state conditions with and without the secondary air system in operation were run under identical operating conditions. Upon completion of testing at the five speeds, the data was tabulated and checked.

Due to the time required to complete the testing over the California seven-mode cycle, it was not possible to run tests with and without the secondary air system during the same test period. Tests number two and three were run on separate days.

A driver was used to operate the vehicle through the California cycle. Once preliminary operations were completed and the driver was able to follow the seven-mode cycle within the one mile per hour and one second specifications, the test runs were begun. With the vehicle in gear and the rear wheels locked, the NDIR analyzers, flame ionization analyzer, and NO_x sampling train were connected to the sampling probes and the recorders started. The tape recorder was started, the driver listening to instructions through a headset. At the beginning of the idle mode, the driver simultaneously pushed a button to place a pip on the recorders and honked the horn. At the sound of the horn, a stop watch used to indicate NO_x grab sampling time, was started. The first grab sample was taken during the idle mode. Successive samples were taken at five second intervals throughout the cycle. Each sample, similar to steady state testing, required 25 to 30 minutes for sampling, analyzing, and preparing the analyzer for the next sample. Each sample period consisted of a minimum of 23 separate runs. A complete cycle was made for each run, the NDIR and flame ionization units giving continuous analysis, thus serving as a repeatability check of the cycle. If the recorder trace for one run did not agree with those for previous runs, or if the driver felt he had not operated the vehicle within the specifications, the test was rerun. Only one temperature record was made for each run, since only one recorder was available. However, during each test, several runs were recorded at each thermocouple.

Upon completing the experimental work with the rich limit carburetor, the lean limit carburetor was installed on the engine. A repeat of the above tests was made with the lean carburetor. The flow characteristics of the air pump were also determined using an integrating commercial gas meter.

This completed the experimental work that was carried out. The results are presented in the following section.

V. RESULTS

The results of this work are presented in Figures 9 to 12 and Tables 2 to 5. Sample calculations are included in the Appendices.

Table 2 lists the results of the steady state constant speed testing with the rich carburetor. Data are listed for operation with and without the secondary air injection system connected. The airfuel ratio at idle was determined from NDIR measurements to be 13.8 to 1. Data corrected for dilution by the secondary air are also presented. Air dilution correction factors were calculated using exhaust gas flow rate measurements and by a carbon balance. Details of these calculations are included in Appendix B.

Table 3 presents the results of the steady state constant speed testing with the lean carburetor. The air-fuel ratio at idle as determined from NDIR measurements was 17 to 1.

Figures 9 and 10 are plots of the oxides of nitrogen emission concentrations during the California cycle with and without the air system in operation for both carburetors. Results with the air system in operation were corrected for air dilution by a carbon balance, details of which are included in Appendix B. Each data point was plotted in the center of the three second time period required to pull the sample, as indicated by the bars on each side of the data points.

Speed	Without Air Injection System			With Air Injection System							
	····			<u></u>	<u></u>	·	<u> </u>	<u></u>	Corrected for Dilution		
	HC	СО	CO2	NO _x	HC	СО	CO2	NO _x	HC	СО	NOx
10 mph	1000	2.4	14.7	0	120	0.5	12.6	0	154	0.6	0
20 mph	1000	1.9	14.0	72.5	70	0.2	12.1	110	91	0,3	143
30 mph	1050	2.5	13.9	455	80	0.4	12.1	540	100	0.5	675
40 mph	1900	1.5	14.7	975	135	1.1	12.9	900	162	1,3	1080
50 mph	1050	1.5	13.4	1025	135	1.2	12.1	1345	158	1.4	1573

Table 2. Exhaust gas analysis, with and without air injection system, steady state conditions rich mixture.

Hydrocarbons - ppm as n-hexane NO_x - ppm CO and CO_2 percent by volume

Speed	Without Air Injection System			With Air Injection System							
	······		,,	<u></u>		<u></u>			Corrected for Dilution		
	HC	СО	со ₂	NOx	HC	СО	CO2	NOx	HC	СО	NOx
10 mph	200	0	14.1	105	145	0	10.4	90	183	0	113
20 mph	160	0.2	13.6	145	100	0	11.1	165	124	0	205
30 mph	180	0.1	13.8	500	125	0.1	11,2	337	153	0,1	610
40 mph	250	0.3	14.0	1390	120	0.2	12.0	1285	139	0.2	1610
50 mph	160	0.3	14.4	1900	80	0.3	13.0	1700	88	0.3	1870

Table 3. Exhaust gas analysis, with and without air injection system, steady state conditions, lean mixture.

Hydrocarbons - ppm as n-hexane NO_x - ppm CO and CO_2 - percent by volume



Figure 9. Oxides of Nitrogen Emission Concentrations during the California Seven-Mode Cycle, with and without Air Injection System for Rich Mixture.



Figure 10. Oxides of Nitrogen Emission Concentrations During the California Seven-Mode Cycle, With and Without Air Injection System for Lean Mixture.

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The weighted average concentrations of unburned hydrocarbons, carbon monoxide, and carbon dioxide, with and without the air system in operation, during the California seven-mode cycle are presented in Tables 4 and 5. All concentrations listed were determined in accordance with California code. To remove the dilution effect of the added air, all concentrations were corrected to 15 percent carbon in the exhaust. The concentrations for each mode are an average of that determined from four typical runs during the test period.

Figures 11 and 12 are plots of exhaust gas temperatures in the exhaust manifold and tailpipe during the California cycle, with and without the air injection system in operation. The temperatures shown for the exhaust manifold occurred at the point measuring exhaust from one cylinder. The temperature at thermocouple number 2, measuring the temperature of the exhaust from four cylinders, followed the same curve as that shown for thermocouple number 1, but was 20 to 100 degrees lower.

A repeatability determination for the NO_x analyzer was made at 30 mph steady state conditions with the rich carburetor. The air injection system was not connected. Five samples were taken and analyzed, giving an average reading of 400 ppm with a variation of ± 20 ppm or ± 5 percent.

The Appendices include the following:

	Without A	Air Injection	System	With Air Injection System			
		CO	CO ₂		CO	CO2	
Mode	HC ppm	Percent	Percent	HC ppm	Percent	Percent	
Idle	350	1.94	13.08	248	0.52	14.47	
0-30 mph	347	1.33	13.62	250	0.64	14.39	
30 mph	2 18	0.89	14.12	148	0.41	14.57	
30-15 mph	1150	2.28	12.00	332	0,30	14.51	
15 mph	376	2.29	12.78	154	0.53	14.46	
15-50 mph	370	1.59	13.43	233	0.48	14.46	
50-20 mph	1700	2.28	11,50	907	0.24	14.19	
Weighted Average	433	1.56		250	0.50		

Table 4. California seven-mode cycle exhaust gas analysis, rich mixture.

All data corrected to 15 percent carbon in exhaust.

	Without 4	Air Injection	System	With Air Injection System			
	<u></u>	СО	CO ₂		СО	CO2	
Mode	HC ppm	Percent	Percent	HC ppm	Percent	Percent	
Idle	298	0	15.0	245	0	15.0	
0-30 mph	286	0.05	14,95	237	0.05	14.93	
30 mph	173	0.08	14.92	151	0.14	14.86	
30-15 mph	1900	0.42	13.39	1734	0.16	13,80	
15 mph	421	0.46	14.56	282	0.27	14.78	
15-50 mph	352	0.27	14.79	294	0.26	14.82	
50-20 mph	2940	0.67	12.56	1870	0.24	13.66	
Weighted Average	493	0.21		396	0.17		

Table 5. California seven-mode cycle exhaust gas analysis, lean mixture.

All data corrected to 15 percent carbon in exhaust.



Figure 11. Exhaust Gas Temperatures During California Seven Mode Cycle; Rich Mixture.

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Figure 12. Exhaust Gas Temperatures During California Seven-Mode Cycle, Lean Mixtures.

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1) Appendix A is a theoretical equilibrium calculation of the oxides of nitrogen formation in the exhaust manifold.

2) Appendix B includes sample calculations of the two methods used to determine air dilution correction factors: exhaust gas flow measurement and a carbon balance.

3) Appendix C includes sample steady state calculations, calibration curves for the analyzers, and sample calculations of calibration blends for the NO_x analyzer.

4) Appendix D includes a description of the California sevenmode cycle and the flow characteristic curves for the air pump.

The results obtained are discussed in the section which follows.

VI. DISCUSSION OF RESULTS

Steady State Operation

Analysis of the results of the steady state constant speed testing presented in Tables 2 and 3 indicates that the secondary air system was more effective in reducing hydrocarbon and CO emissions when the engine was operating with the rich carburetor. With the rich carburetor installed on the engine, a maximum of 85 to 90 percent reduction of the unburned hydrocarbon emissions and a maximum of 85 percent reduction of CO emissions were obtained by operation of the secondary air injection system. With the lean carburetor installed on the engine, the maximum hydrocarbon reduction was 50 percent, and only a small decrease in carbon monoxide occurred. However, final concentrations of hydrocarbons in the exhaust with the secondary air system operating were about the same for both carburetors; the final concentration of CO being much less with the lean carburetor.

The oxides of nitrogen emissions in the exhaust were greater at constant speeds for engine operation with the lean carburetor. The NO_x concentrations, for both rich and lean operation, increased with speed. The increase in NO_x concentrations with speed would indicate higher combustion temperatures and/or leaner air-fuel mixtures with an increase in speed (35, p. 737). Carbon monoxide and carbon dioxide concentrations did not indicate leaner mixtures at higher speeds in all cases, but exhaust gas temperatures measured during the tests were greater at higher speeds, indicating higher peak cyclic temperatures.

During operation with the rich carburetor, an increase in NO_x emissions due to the introduction of the secondary air at the exhaust port occurred at all speeds except ten mph. A maximum increase of 500 ppm occurred at 50 mph. For lean mixture operation, increases in NO_x emissions by the introduction of secondary air were observed at all speeds except 50 mph. The maximum was less than that for the rich carburetor however: 220 ppm at 40 mph.

The results obtained for lean carburetion at 50 mph agree fairly well with the theoretical results calculated earlier. Theoretically, ten ppm would be formed at equilibrium, while actual measurements showed a decrease of 30 ppm. Difference between these two amounts at the concentrations being measured is not significant, considering the repeatability of the sample analysis. However, results at other speeds would not be predicted using equilibrium and kinetic formation rate calculations for temperatures measured in the exhaust manifold. Experiments carried out for the formation of NO_x in gas-fired heaters produced the same problem of correlation with theoretical calculations (9, p. 19). The results obtained would indicate that the secondary air was increasing in temperature to 3000° F or higher at the exhaust port, as discussed earlier in the theory section, or that the production of NO was not occurring by the homogeneous formation reaction.

The two carburetors used during this study were calibrated on a carburetor test stand to operate at the rich and lean limits obtained from a normal distribution curve of the operation of carburetors installed on manufactured automobiles. Installed on the engine, however, the carburetors gave leaner operation than was desired. Air-fuel ratios leaner than desired with the carburetors were due to (1) difference between conditions imposed on the carburetors installed on the engine and those during calibration, i.e., pressure drop across the venturi versus throttle opening, and (2) operating the engine without the air cleaner, thus allowing more air to enter the carburetor.

Correction Factors for Air Dilution

Exhaust gas analyses were made with the hydrogen flame ionization detector to determine the total hydrocarbon concentration of the exhaust for use in calculation of dilution correction factors by a carbon balance. However, the results obtained with the analyzer were unsatisfactory and not usable for calculations. The measurement delay time from the engine to the instrument, 16 seconds, was too long to accurately measure concentrations during the California cycle. The samples for steady state constant speed operation were contaminated by carbon particulate and condensed water vapor in the sampling train. The water and particulate build up was due to the sampling lines being too long and the sample flow rate too slow. Noise in the electrical system of the instrument made recorder deflections difficult to interpret.

Since the results of the flame ionization analyzer were not satisfactory, hydrocarbon concentrations measured by the NDIR analyzer were used in computing the carbon balance. Two assumptions were made in converting the instrument reading to hydrocarbon percentage in the exhaust: (1) all hydrocarbons have six carbon atoms, and (2) that the ratio of total hydrocarbons to hydrocarbons measured by a NDIR analyzer is 1.5. Although it has been shown that the ratio of total hydrocarbons to those measured by a NDIR analyzer is not a constant, the average value of the ratio is 1.5 (22, p. 26). With the relatively low hydrocarbon emissions of this test vehicle, a factor from 1.5 to 2 could have been used without a material effect on the dilution factors computed from the carbon balance.

The dilution factors determined by the exhaust gas flow rate measurements with the Pitot tube agreed well with those determined by the carbon balance. Care must be exercised during flow

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measurements to assure that pressures are measured at the same points during each traverse.

California Cycle Operation

The oxides of nitrogen emissions from the test vehicle operating on the California seven-mode cycle with and without the secondary air system in operation for both rich and lean carburetors are shown in Figures 9 and 10. The data points, plotted at the center of the three second sampling period, were connected by curves located at the discretion of the author. It is not the purpose of the curves to indicate the NO_x concentration at any specific time during the cycle, but to allow the results to be more easily followed through the cycle.

The oxides of nitrogen emissions of the engine were low during the idle, 15 mph cruise, and deceleration modes. During these conditions of closed or nearly closed throttle, peak cylinder temperatures and engine air consumption are relatively low. With higher peak cyclic temperatures and leaner mixtures occurring during acceleration, the NO_x emissions increased sharply. As predicted earlier in the theory section of this report, the NO_x emissions with lean carburction were equal to or greater than those with rich carburction, during operation without secondary air.

The injection of secondary air in the exhaust ports of the

engine affected the oxides of nitrogen emissions only during the acceleration modes. The NO_x emissions during both acceleration modes for both carburetors were increased by the injection of secondary air into the exhaust ports. A larger increase in NO_x emissions observed with the rich carburetor correlates with the better oxidation of hydrocarbons and carbon monoxide by the secondary air during operation with the rich carburetor. The heat produced by the oxidation process appears to be instrumental in the production of the oxides of nitrogen. During operation with the rich carburetor, an increase of 800 ppm or 40 percent in NO_x concentration due to the secondary air was observed during the second acceleration mode of the California cycle.

No attempt was made to determine the weighted average concentration of NO_x over the California cycle. Since the curves drawn connecting the data points of this study can be shifted within the three second sampling periods, determinations of average mode concentrations from these curves would not be accurate. A continuous analysis would be necessary to obtain the actual curve of the NO_x concentration versus time which could be used to determine the average mode concentrations.

The grab sampling method used to obtain NO_x samples worked well. A repeatability check of the method was not made during California cycle operations, however a check made during steady state operation showed the repeatability of the analysis to be within <u>+</u> five percent. Nicksic and Harkins showed results determined by the spectrophotometric method of analysis to be comparable to those obtained by the conventional phenoldisulfonic acid method (8, p. 987).

The NO_x concentrations should have changed more sharply at the beginning and end of modes than is observed in Figures 9 and 10. There appears to have been mixing of the exhaust from the end of one mode and the beginning of the next mode in the exhaust pipe, causing carry-over of concentrations from the previous mode, i.e., NO_x concentrations measured during deceleration. The three second sampling period also contributed to the less distinct changes in concentrations. To obtain more accurate NO_x concentrations at the beginning and end of modes, the samples should be taken from the exhaust pipe closer to the engine and during a shorter time period.

Emission concentrations of unburned hydrocarbons, carbon monoxide, and carbon dioxide during the California seven-mode cycle, with and without the secondary air injection system in operation are presented in Tables 4 and 5. The concentrations were determined in accordance with California specifications (5, pt. 1, p. 15-18). The hydrocarbon and carbon monoxide emissions were much lower than that of the average car (19, p. 327). The secondary air system proved effective in reducing concentrations to within the California standards during operation with the rich carburetor, but did not reduce the hydrocarbon emissions to the standard during operation with the lean carburetor. Apparently too much secondary air was being injected into the exhaust ports for effective hydrocarbon reduction during operation with the lean carburetor. The reduction of hydrocarbons and carbon monoxide during the second acceleration with the rich carburetor, discussed earlier, can be observed in Table 4.

Exhaust Gas Temperatures

Exhaust gas temperatures during the California seven-mode cycle, plotted in Figures 11 and 12, as measured by a thermocouple located in the exhaust manifold, were greatest during acceleration and 30 mph cruise conditions. There was no appreciable difference in temperatures measured during operation with the rich and the lean carburetors. Except during decelerations and 15 mph cruise with the rich carburetor, there was no increase in exhaust gas temperature measured in the exhaust manifold with the addition of secondary air. However, there was also very little decrease which gives indication that the oxidation reactions might be occurring, providing energy to heat the secondary air to the exhaust gas temperature. An increase of 75 to 100° F was observed during deceleration and 15 mph cruise with the rich carburetor.

The exhaust gas temperatures measured at the end of the

tailpipe were higher during the operation of the secondary air system. Assuming the same heat loss from the exhaust system during operation with or without the secondary air, the increase in mass flow rate due to the secondary air decreased the temperature change of the exhaust gases through the system, resulting in higher temperatures at the end of the tailpipe.

During steady state testing, an attempt was made to obtain a correction factor for the radiation loss of thermocouple number one by replacing it with a shielded thermocouple. Although corrections were obtained for the specific conditions of each test, results showed no trend which could be applied to the transient data. The temperatures measured with the shielded thermocouple were the same as, to 120° F lower than those measured with the bare-wire thermocouple, depending on speed, carburetor, and whether the secondary air system was operating. The temperature results presented in Figures 11 and 12 are as indicated by the bare-wire thermocouples.

VII. CONCLUSIONS

Conclusions drawn from the results of testing the secondary air injection system mounted on the test vehicle are as follows:

1) The addition of secondary air at the exhaust ports increased the oxides of nitrogen emissions during acceleration for both rich and lean mixture operation. As high as 40 percent increase occurred during operation with the rich carburetor. Appreciable increase also occurred during high speed steady state cruise conditions with the rich carburetor. Weighted average concentrations of NO_x for operation on the California cycle were not determined.

2) The grab sampling and spectrophotometric analysis methods for the oxides of nitrogen worked well during the testing. However, the time required to take a grab sample, three seconds, was too long to obtain instantaneous analysis. Sampling probes should be located closer to the engine to avoid mixing of exhaust from separate modes in the exhaust pipe prior to analysis.

3) Temperatures in the exhaust manifold were not markedly changed by the injection of secondary air into the exhaust ports. However, temperatures were 50 to 100° F higher at the end of the tailpipe due to increased exhaust gas mass flow rate.

4) The vehicle with the secondary air system installed met
California standards for operation with the rich carburetor, but emitted a higher concentration of unburned hydrocarbons than the standard during operation with the lean carburetor.

VIII. RECOMMENDATIONS

From experience gained during this study, the following recommendations for continuing work in this area are included.

1) Repeat the tests for several representative vehicles.

2) Use of the hydrogen flame ionization detector is desirable to determine total hydrocarbon concentration. Upgrading of this sampling system to include a shorter sampling train and faster sampling flow rate should be accomplished.

 The use of a device to measure exhaust flow rates is desirable. A viscous flow meter described by Neerman and Millar (27, p. 2), would be acceptable.

4) To obtain better repeatability during operation of the California cycle, by eliminating the human factor, the engine controller discussed earlier or one of similar design should be adapted to the test vehicle.

5) A rich limit carburetor should be included with the two used during this test to give results over the full range of intake mixtures.

6) A method should be devised to shorten the grab sampling time to obtain a more instantaneous NO_x sample.

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IX. BIBLIOGRAPHY

- Addicott, Donald James. Partial recirculation of diesel exhaust for the reduction of oxides of nitrogen. Master's thesis. Corvallis, Oregon State University, 1964. 54 numb. leaves.
- Bishop, J. W. and G. J. Nebel. Control of oxides of nitrogen in automobile exhaust gases. AMA Archives of Industrial Health 17:511-518. 1958.
- Brownson, D. A., R. S. Johnson and A. Candelise. A progress report on manifold air oxidation of exhaust gas.
 Paper presented at the SAE National Automobile Week Meeting, Detroit, 1962. New York, 1962. 16 p. (Society of Automotive Engineers Paper 486N)
- California. Motor Vehicle Pollution Control Board. The auto smog story. Biennial Report. Presented to Governor Edmund G. Brown and the State Legislature, Jan., 1965. 20 p.
- California test procedure and criteria for motor vehicle emission control. Rev. ed. Los Angeles, 1964. 57 p.
- Callahan, Joseph M. Crash program for smog pump. Automotive News (Detroit, Michigan) p. 18, col. 2-3-4-5. Feb. 22, 1965.
- Chandler, J. M., A. M. Smith and J. H. Struck. Development of the concept of nonflame exhaust gas reactors. Paper presented at the SAE National Automobile Week Meeting, Detroit, 1962. New York, 1962. 41 p. (Society of Automotive Engineers Paper 486M)
- Clayton Manufacturing Company. Model C-41 vehicle analyzer dynamometer instruction manual. El Monte, Calif., 1941.
 69 p.
- Connolly, T. J. and K. Nobe. The formation of oxides of nitrogen in gas-fired heaters. Los Angeles, 1955. 25 p. (UCLA Department of Engineering. Report 55-27)

- Daniels, Farrington and Nathan Gilbert. Fixation of atmospheric nitrogen in a gas heated furnace. Industrial and Engineering Chemistry 40:1719-1723. 1948.
- Daniels, Farrington. Nitrogen oxides and development of chemical kinetics. Chemical and Engineering News 33:2370-2373. 1955.
- Faith, W. L. Nitrogen oxides. Chemical Engineering Progress 52:342-344. 1956.
- Haagen Smit, A. J. Photochemistry and smog. Journal of the Air Pollution Control Association 13:444-447. 1963.
- 14. The control of air pollution. Scientific American 210:25-31. 1964.
- Hass, G. C. The California motor vehicle emission standards. Paper presented at SAE National West Coast Meeting, San Francisco, Aug., 1960. New York, 1960. 6 p. (Society of Automotive Engineers Paper 210A)
- 16. Heinen, C. M. Thermal considerations in exhaust emission control systems. Paper presented at the SAE National Automobile Week Meeting, Detroit, 1962. New York, 1962.
 24 p. (Society of Automotive Engineers Paper 436J)
- Hurn, R. W. Comprehensive analysis of automotive exhausts. Archives of Environmental Health 5:592-596. 1962.
- 18. Jaros, Gary Dean and Neill R. Parkin. The fate of oxides of nitrogen through a direct flame afterburner in the exhaust of a gasoline engine. Master's thesis. Corvallis, Oregon State University, 1964. 68 numb. leaves.
- Jensen, Donald A. et al. Sources and kinds of contaminants from motor vehicles. Journal of the Air Pollution Control Association 14:327-328. 1964.
- Johnson, Douglas Edward. A rapid method for determination of nitrogen oxides in engine exhaust gas. Master's thesis. Corvallis, Oregon State University, 1962. 48 numb. leaves.

- 21. Kreith, Frank. Principles of heat transfer. Scranton, International Textbook Company, 1958. 553 p.
- Lepisto, Paul R. et al. Hydrocarbon emissions from automobiles. Los Angeles, 1961. 45 p. (Air Pollution Foundation Report no. 32)
- Maga, John A. Air quality and motor vehicle emission standards for oxides of nitrogen. Presented to California Motor Vehicle Pollution Control Board, San Francisco, June 5, 1963. 6 p. (Processed)
- Messersmith, C. W., C. F. Warner and R. A. Olsen. Mechanical engineering laboratory. 2d ed. New York, Wiley, 1960. 179 p.
- 25. Mills, John L. et al. Emissions of oxides of nitrogen from stationary sources in Los Angeles County. Los Angeles, 1961. 33 p. (Los Angeles County Air Pollution Control Board Report, no. 4)
- 26. Morris, Robert A. and Robert L. Chapman. Flame ionization hydrocarbon analyzer. Journal of the Air Pollution Control Association 11:467-469, 489. 1961.
- 27. Neerman, J. C. and G. H. Millar. Determination of hydrocarbon emission rate by continuous air flow measurement and exhaust analysis. Paper presented at SAE National West Coast Meeting, Seattle, Aug., 1957. New York, 1957. 11 p. (Society of Automotive Engineers Paper 168)
- Nicksic, S. W. and J. Harkins. Spectrophotometric determination of nitrogen oxides in auto exhaust. Analytical Chemistry 34:985-988. 1962.
- Smith, J. M. and H. C. Van Ness. Chemical engineering thermodynamics. 2d ed. New York, McGraw-Hill, 1959. 490 p.
- 30. Smog control. Product Engineering 35:44-45. Aug. 31, 1964.
- 31. Summer approval sought for exhaust controls. Chemical and Engineering News 42:80-86. Mar. 9, 1964.

- 32. Taylor, C. Fayette and Edward S. Taylor. The internal combustion engine. Rev. ed. Scranton, International Textbook Co., 1956. 339 p.
- 33. The internal combustion engine. 2d ed. Scranton, International Textbook Co., 1961. 668 p.
- 34. Vickland, C. W. et al. A consideration of the high temperature thermodynamics of internal combustion engines. Paper presented at SAE summer meeting, St. Louis, 1961. New York, 1961. 10 p. (Society of Automotive Engineers Paper 380A)
- 35. Wimmer, D. B. and L. A. McReynolds. Nitrogen oxides and engine combustion. Paper presented at SAE summer meeting, St. Louis, 1961. New York, 1961. 15 p. (Society of Automotive Engineers Paper 380E)

APPENDICES

APPENDIX A

General

This appendix includes a theoretical calculation of the oxides of nitrogen which could be formed in the exhaust manifold when the secondary air injection system is in operation on the vehicle.

During testing thermocouples indicated temperatures as high as 1300° F in the exhaust manifold. This occurred during the 50 mph steady state cruise condition with the lean carburetor.

The engine exhaust flow rate measured at exhaust temperatures was found to be 160 cfm without the injection system in operation and 180 cfm with the system operating. Without the system in operation, the volume percent of carbon monoxide was 0.4 percent, which would place the air-fuel ratio close to stoichiometric. Thus the engine exhaust consists of negligible oxygen and approximately 80 percent nitrogen. The 20 cfm which is introduced by the air system consists of 79 percent nitrogen and 21 percent oxygen by volume.

Assuming that none of the oxygen combines with the hydrocarbons or carbon monoxide in the exhaust, the mole fractions of nitrogen, oxygen, and other constituents are calculated as follows:

$$\frac{\text{Mole N}_2}{\text{Mole exhaust gas}} = \frac{(0.80)(160 \text{ cfm}) + (0.79)(20 \text{ cfm})}{180 \text{ cfm}}$$

$$= \frac{0.80}{180 \text{ cfm}}$$

$$\frac{\text{Mole O}_2}{\text{Mole exhaust gas}} = \frac{(0.21)(20 \text{ cfm})}{180 \text{ cfm}}$$

$$= 0.024$$

$$\frac{\text{Mole other constituents}}{\text{Mole exhaust gas}} = 1 - 0.80 - 0.024$$

$$= 0.176$$

Equilibrium Constants

The three reactions which might be significant in producing oxides of nitrogen in the exhaust manifold are as follows (9, p. 5):

$$1/2 N_2 + 1/2 O_2 = NO$$
 (1)

$$1/2 N_2 + O_2 = NO_2$$
 (2)

$$NO + 1/2 O_2 = NO_2$$
 (3)

The equilibrium constant at 1300° F for reaction (1) is calculated using the following three equations (29, p. 412):

$$\Delta H_{0} = \Delta H^{0} - \Delta \alpha T - \frac{\Delta \beta T^{2}}{2} - \frac{\Delta \gamma T^{3}}{3}$$
$$\Delta F^{0} = \Delta H_{0} - \Delta \alpha T \ln T - \frac{\Delta \beta T^{2}}{2} - \frac{\Delta \gamma T^{3}}{6} - IT$$
$$\ln K = -\frac{\Delta H_{0}}{RT} + \frac{\Delta \alpha \ln T}{R} + \frac{\Delta \beta T}{2R} + \frac{\Delta \gamma T^{2}}{6R} + C$$

where

$$\Delta \alpha$$
, $\Delta \beta$, and $\Delta \gamma$ = specific heat constants
 ΔH_0 = constant

 $\Delta H^{O} = \text{standard heat of reaction}$ $\Delta F^{O} = \text{standard free energy change}$ K = equilibrium constant $C, I = \text{constants } C = \frac{I}{R}$ $T = \text{temperature, } ^{O}K$ R = universal gas constant

Values for $\Delta \alpha$, $\Delta \beta$, Δ^{γ} , ΔH^{O} , and ΔF^{O} were taken from tables in Smith and Van Ness (29) pages 122, 138, and 417 respectively.

Values of the equilibrium constants for reactions (2) and (3) were taken from data published by Connolly and Nobe (9, p. 6).

The equilibrium constants for the three reactions at 1300° F are:

$$K_1 = 6.9 \times 10^{-5}$$

$$K_2 = 7.6 \times 10^{-6}$$

$$K_3 = 1.22 \times 10^{-1}$$

Equilibrium Concentrations

Knowing the values for the equilibrium constants, the equilibrium concentrations of NO and NO_2 can be calculated. Since the reactions are not independent of each other, three equations with three unknowns will be solved. The table that follows lists the initial moles, moles formed, and moles at equilibrium for each constituent.

Constituent	Initial Moles	Moles Formed	Moles at Equilibrium	
N ₂	0.80	-a -b	0.80 - a - b	
02	0.024	-a -2b -c	0.024 - a - 2b - c	
NO	0	2a - 2c	2a - 2c	
NO ₂	0	2b + 2c	2b + 2c	
Other	0.176	0	0.176	
	1.00		l-b-c	

Table A-1. Moles of constituents.

Where a, b, and c are unknowns

The equilibrium constant may be calculated from the formula

(29, p. 421):

 $K = K_{\phi} K_{\gamma} K_{\gamma} p^{(c+d-a-b)}$

Where

K_φ = ratio of fugacity coefficients
K_Y = ratio of activity coefficients
K_y = ratio of the mole fractions
p = total pressure
c & d = moles of products shown in equilibrium formula, not the same as unknowns shown in Table A-1.
a & b = moles of reactants shown in equilibrium formula, not the same as unknowns shown in Table A-1.

The total pressure in the exhaust manifold is assumed to be 1 atm, and the exhaust gases are assumed to act as perfect gases in an ideal solution. Thus

$$p = K_{\phi} = K_{\gamma} = 1$$
$$K = K_{y} = \frac{y_{C}^{c} y_{D}^{d}}{y_{A}^{a} y_{B}^{b}}$$

Where

- y = mole fraction
- C & D identify products
- A & B identify reactants

The equations for the three reactions are as follows:

$$K_{1} = \frac{y_{NO}}{\sqrt{y_{O_{2}} y_{N_{2}}}}$$
$$K_{2} = \frac{y_{NO_{2}}}{y_{O_{2}} \sqrt{y_{N_{2}}}}$$
$$K_{3} = \frac{y_{NO_{2}}}{y_{NO} \sqrt{y_{O_{2}}}}$$

Substituting the mole fractions from Table A-l into the above, the equations become:

$$6.9 \times 10^{-5} = \frac{2(a-c)}{\sqrt{(0.024 - a - 2b - c)(0.80 - a - b)}}$$

$$7.6 \times 10^{-6} = \frac{2(b+c)\sqrt{1-b-c}}{(0.024 - a - 2b - c)\sqrt{0.80 - a - b}}$$

$$1.22 \times 10^{-1} = \frac{2(b-c)\sqrt{1-b-c}}{2(a-c)\sqrt{(0.024 - a - 2b - c)}}$$

Solving by trial and error, the values of a, b, and c are obtained:

a =
$$4.77 \times 10^{-6}$$

b = 8.15×10^{-8}
c = 8.80×10^{-8}

From Table A-1, the equilibrium concentrations of NO and NO_2 at 1300° F are:

$$NO = 9.5 ppm$$

$$NO_2 = 0.17 \text{ ppm}$$

APPENDIX B

Two methods were used to correct the gas concentrations in the exhaust for dilution by the secondary air: exhaust gas flow rate measurement and a carbon balance. Exhaust gas flow rate measurements were made using a Pitot tube located at the end of the tailpipe. The Pitot tube measurements could be made only during steady state operation. Carbon balance calculations were made for both steady state and California cycle conditions.

Sample calculations of each method are included for the constant speed steady state condition of 50 mph with the lean carburetor.

Flow Rate Measurement

For incompressible fluids, the velocity measured by the Pitot tube was computed from the equation (31, p. 71):

$$\overline{V} = C \sqrt{2g_c} \frac{\Delta p}{\rho}$$

where

 \overline{V} = fluid velocity, ft/sec.

C = 0.98 to 1.02

- Δp = impact pressure minus static pressure as measured by the Pitot tube, $1b/ft^2$
- ρ = fluid density, lb/ft³

$$g_c = 32.2 \frac{\text{ft-lbm}}{\text{sec}^2-\text{lbf}}$$

The correction for compressible fluids is less than one percent for velocities less than 300 feet per second.

Once the average velocity is determined, the flow rate was computed from the equation:

$$Q = A \overline{V}$$

where

Q = flow rate, ft^3/min A = area of pipe, ft^2 \overline{V} = average velocity, ft/sec

The area of the exhaust pipe was 0.0308 square feet.

The density of the exhaust gas was assumed to be the same as for air at the same temperature. The temperatures were determined from data at thermocouple number three. The Δp in the velocity equation is an average value determined by a traverse of the exhaust pipe cross-sectional area. Sample calculations for flow rates with and without the secondary air system in operation are included below.

at 30 mph without secondary air

T = 345° F ρ = 0.0493 lb/ft³ (32, p. 535) Δp = (0.107 in. H₂O) (5.20 psf/in. H₂O) = 0.556 psf

$$\overline{V} = \sqrt{\frac{(2)(32.2)(0.556)}{(0.0493)}} = \sqrt{727} = 27 \text{ ft/sec}$$

$$Q = (0.0308 \text{ ft}^2)(27 \text{ ft/sec})(60 \text{ sec/min}) = \frac{50 \text{ cfm}}{50 \text{ cfm}}$$
at 30 mph with secondary air

$$T = 370^{\circ} \text{ F}$$

$$\rho = 0.0478 \text{ lb/ft}^3$$

$$p = (0.156 \text{ in. H}_2\text{O})(5.20 \text{ psf/in. H}_2\text{O}) = 0.811 \text{ psf}$$

$$\overline{V} = \sqrt{\frac{(64.4)(0.811)}{(0.0478)}} = \sqrt{1092} = 33.1 \text{ ft/sec}$$

$$Q = (0.0308 \text{ ft}^2)(33.1 \text{ ft/sec})(60 \text{ sec/min}) = \frac{61.1 \text{ cfm}}{50 \text{ cfm}}$$
Dilution correction factor = $\frac{\text{With air flow rate}}{\text{Without air flow rate}}$

$$= \frac{61.1 \text{ cfm}}{50 \text{ cfm}}$$

$$= 1.22$$

Carbon Balance

The carbon balance was made with the results obtained from the NDIR analyzers: CO, CO₂ and unburned hydrocarbon concentrations, with and without secondary air. The CO and CO₂ data were multiplied by 1.05 to convert them to a dry basis. This assumes saturated gas at 90° F in the analyzer. No water vapor correction was made for the hydrocarbon readings since the wet CO₂ filter cell was included in the analyzer.

The correction factor was then determined from the

following equation:

Dilution correction factor =
$$\frac{\% HC + \% CO + \% CO_2 \text{ (Without air)}}{\% HC + \% CO + \% CO_2 \text{ (With air)}}$$

The percent hydrocarbons was determined by multiplying the analyzer reading by six to account for the carbon atoms, and then by a factor of 1.5 to account for hydrocarbons not analyzed by the NDIR instrument (13, p. 26; 33, p. 8). Sample calculations for the dilution correction factor are included as follows:

at 30 mph without secondary air

 $CO\% = 0.10 \times 1.05 = 0.11$

 $CO_2\% = 13.1 \times 1.05 = 13.80$

 $HC\% = 0.0180 \times 6 \times 1.5 = 0.16$

at 30 mph with secondary air

 $CO\% = 0.1 \times 1.05 = 0.11$ $CO_2\% = 10.65 \times 1.05 = 11.20$ $HC\% = 0.0125 \times 6 \times 1.5 = 0.11$ Dilution correction factor = $\frac{0.16 + 13.80 + 0.11}{0.11 + 11.20 + 0.11}$

APPENDIX C

Constant Speed Steady State Data Correlation

The carbon monoxide and carbon dioxide data reported for steady state conditions was converted to a dry basis. A factor of 1.05 was applied for conversion; this assumes saturated gas at 90° F in the analyzer.

The water vapor correction for the unburned hydrocarbon concentrations was considered negligible, since the filter cell was installed in the analyzer.

Infrared Analyzer Calibration

The three non-dispersive infrared analyzers were calibrated by flowing gases with known concentrations of CO, CO_2 , and n-hexane through the instruments to determine the recorder deflections. Nitrogen was used as the zeroing gas.

The gas blends which were used are listed in Table C-1. The concentration of gases in the blends were determined from a number of sources. Blends number one and two were made by diluting known gases with nitrogen, the actual concentrations being determined by gas chromatography. Blends number four and five were gas blends purchased from the Matheson Company, Inc. The

	Composition, Percent by Volume in Nitrogen				
Blend	CO	CO ₂	n-hexane		
1	-	-	0,0700		
2	5.0	8.0	0.1000		
3	8.0	12.1	0.1595		
4	9.4	14.5	0.2900		
5	-	-	0.6300		
6	3.0	9.8	-		

Table C-1. Calibration gases for NDIR analyzers.

actual concentrations in blend number four were determined through the courtesy of the Scott Research Laboratories, Inc. The hydrocarbon concentration in Blend number five was determined by gas chromatography. Blends number three and six were gas blends furnished by the Scott Research Laboratories, Inc. through its gas blend cross reference service.

The resulting calibration curves are plotted in Figure C-1.

$NO_{\mathbf{x}}$ Calibration Gas Determination

The following is a sample calculation of the NO concentration of a calibration gas for the NO_x spectrophotometer.

Volume of blending flask = 2175 ml

Volume of NO injected into flask = 1.5 ml



Figure C-1. Non Dispensive Infared Analyzer Calibration Curves.

Flask then filled to atmospheric pressure with nitrogen

Sample concentration =
$$\frac{1.5 \text{ ml}}{2175 \text{ ml}}$$
 = $\frac{690 \text{ ppm}}{2175 \text{ ml}}$

The NO_x spectrophotometer was calibrated as discussed in the Procedure section. The calibration curves are shown in Figure C-2.

Flame Ionization Detector Calibration

The response of the flame ionization detector was assumed to be linear with carbon concentration excluding CO and CO_2 , thus requiring only one calibration gas. The gas blend used was blend number three shown in Table C-1.

The pressure at the sample inlet of the instrument was measured with a water manometer, and held constant during calibration and testing to assure the same sample flow rates during each condition. The calibration curves for the two ranges used during testing are shown in Figure C-3. Since the analyzer was originally calibrated to the meter on the instrument, and then the meter calibrated to the recorder, the calibration point for attenuation 50 does not appear on the calibration curve.



Figure C-2. Oxides of Nitrogen Absorption Spectrophotometer Calibration Curves.



Figure C-3. Hydrogen Flame Ionization Detector Calibration Curves.

APPENDIX D

California Seven-Mode Cycle

The California seven-mode driving cycle used for transient test conditions in this work is described in Table D-l (30, pt. l,

p. 3).

Sequence No.	Mode	Acceleration mph/sec	Time in Mode sec	Cumulative Time sec
1	Idle		20	20
2	0-30 mph	2.2	14	34
3	30 mph		15	49
4	30-15 mph	-1.4	11	60
5	15 mph		15	75
6	15-50 mph	1.2	29	104
7	50-20 mph	-1.2	25	129

Table D-1. California seven-mode cycle.

The vehicle did not follow the seventh mode as is specified above for reasons discussed in the Procedure section of this report. A plot of vehicle speed versus time is shown in Figure D-1. The vehicle operation line is coincident with that for the California cycle except during the seventh mode. During the seventh mode, the



Figure D-1. Comparison of Test Cycle to California Seven-Mode Cycle.

 constant deceleration of the California cycle is shown as a dashed line.

Air Pump Characteristics

Typical flow characteristics of the diaphragm air pump used on the secondary air system were supplied by the Ford Motor Company. Discharge flow rates in standard cubic feet per minute versus pump speed for zero back pressure and ten psig back pressure are plotted in Figure D-2.

With the secondary air system connected to the engine, the air flow versus speed was measured with a commercial integrating gas meter connected to the inlet of the pump. As shown in Figure D-2, the flow indication from the gas meter was between the two typical curves. The measured data indicates that the back pressure to the pump increases with speed. This seems reasonable since more exhaust is being discharged into the exhaust manifolds and the pressure drop through the system would be greater with higher flow rates. The indication could also be due to the pressure drop across the flow meter, which was not measured.

The ratio of pump speed to engine speed was found to be 0.88.



Figure D-2. Air Pump Flow Characteristics.